# The Dead Burning of Dolomite

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## DISSERTATION

PRESENTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE GRADUATE SCHOOL OF THE OHIO STATE UNIVERSITY

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BY

JAMES THOMAS ROBSON, B. Ch. E., M. Sc.

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THE OHIO STATE UNIVERSITY
1923

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## PREFACE

This investigation was conducted for the purpose of determining the possibility of utilizing dolomite as a base material in the manufacture of refractories. The work was conducted in coöperation with the U. S. Bureau of Mines, to whom the writer is indebted for the use of equipment and materials. Acknowledgment is also made to Prof. A. S. Watts, Dr. W. J. McCaughey, Mr. G. A. Bole and Dr. J. R. Withrow under whose supervision the work was carried out, for their many valuable suggestions in this work.

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# THE DEAD BURNING OF DOLOMITE.

By James Thomas Robson

## Introduction

Dolomite, a double carbonate of lime and magnesia having the theoretical formula $CaCO_3MgCO_3$, when formed and burned into bricks possesses the undesirable property of disintegrating when standing in the air, due to the slaking of the lime content. Since dolomite is very abundant and possesses great refractoriness together with basic properties similar to magnesite, it is very desirable that this serious slaking defect be overcome so that it may act as a substitute for the more expensive magnesite.

This work was carried on (1) to obtain dolomite in the dead burned form, and (2) to investigate the feasibility of producing standard size bricks of dead-burned dolomite composition.

The term "dead burned" dolomite signifies dolomite which is in the stable form after burning and will not slake down upon prolonged exposure to the atmosphere.

The total apparent consumption of crude magnesite in the United States for 1921, amounted to 113,479 short tons of which 58% was imported.

Normal consumption of magnesite in the United States, in terms of crude, amounts to about 300,000 tons of which a large part is dead burned and consumed by the steel and other metal industries. The year 1921, therefore, resulted in an apparent consumption of but little more than a third of this amount. This was due to the slump in the metal industries.

The entire domestic production of 47,904 tons came from California. That state produces but little dead-burned material, most of the ore being sold as caustic magnesite for other than metallurgical work.

The estimated value per ton of domestic crude ore was $10.65 as against $10.01 for the imported material. The total value of imported magnesite was $525,452 and that of the domestic production $510,177. Of total imports but 6,788 tons were calcined, the remainder 51,993 tons having been brought in as crude. This was probably due to fuel and labor conditions at the point of shipment.

On February 6, 1923, crude magnesite was quoted at $14.00 per ton and calcined magnesite $40.00 per ton f. o. b. California points. The dead-

burned magnesite grains were quoted at $40.00 per net ton f. o. b. at Baltimore and at $40.50 and $42.00 at Chester, Pa. Magnesite bricks, nine-inch straights were quoted at $65.00 and $68.00 per ton f. o. b. the works. At the same time, dolomite one-half inch and larger was quoted at $1.10 and $1.35 per net ton at New York state shipping points.

Magnesite refractories are used in basic open hearth steel furnaces where a number of courses of magnesia brick are used in making the foundation for the bottom, the bottom being made of dead-burned magnesite, and in many cases at present, of granular dolomite. Side walls are built of magnesia brick to a height of about 15 inches above the bottom of the charging doors. They are used around the door jambs and tapping holes, and to face the furnace blocks as a protection to the silica bricks.

Magnesia bricks are used in the construction of soaking pits in the six or eight bottom courses; along the slag line of metal mixers; in the bottom and on the bridge wall of billet and bar heating furnaces; in the bottom side walls and bridge walls of copper reverberatories; in copper converters and special types of furnaces such as silver slimes, dross and bullion furnaces, electrical smelting, heating, welding and melting furnaces, calcium carbide kilns and other furnaces.

## Previous Work

Many attempts have been made to obtain a dead burned dolomite but with varied success. There have been three general lines of procedure employed in these attempts which are as follows:

1. By mixing an impurity with finely ground dolomite and calcining the mixture.[1] The impurities used are: silica, iron oxide, roll scale, flue dust, alumina, chromium oxide, manganese oxide, cobalt oxide, nickel oxide, borax, blast furnace slag, basic open hearth slag, shale, kaolin, coal tar, calcium chloride, magnesium chloride and sodium chloride.

2. By mixing an impurity with coarsely ground dolomite (2–8 mesh) and calcining the mixture.[2] An example of this method is that used in recent times for making sinter dolomite by allowing the grains of dolomite to float about in a bath of molten iron, until the entire grain has encased

[1] G. L. Davison, "Dead Burning Magnesite," U. S. 792,382 June 20 (1905); C. B. Stowe, "Dead Burning Magnesite," U. S. 205,056, Nov. 14 (1916); G. O. Handy and R. M. Isham, "Dead Burning Dolomite," U. S. 1,270,818, July 2 (1918); S. B. Newberry, "Dead Burning Dolomite," U. S. 1,267,686, May 28 (1918); H. G. Schurecht, "Experiments in Dead Burning Dolomite," *J. Am. Ceram. Soc.*, **2** [4], 291 (1919); A. Rollason, "Refractory Substances," Brit. 156,447, April 21 (1920); H. G. Schurecht, "Experiments in Dead Burning Dolomite and Magnesite," *J. Am. Ceram. Soc.*, **4** [2], 127 (1921); C. H. Breeswood, "Dolomite Bricks," U. S. 1,380,701, June 7 (1921).

[2] F. A. Jones, "Process of Producing a Furnace Lining with Dolomite," U. S. 151,535, Jan. 1 (1918); M. Backheuer, "The Preparation of the Dolomite-tar Mixture in Thomas (basic converter) Steel Works," *Stahl u. Eisen*, **41**, 954 (1921).

itself in a protective coating of iron. Also the present used methods for sintering coarse dolomite with basic open hearth slag or other flux come under this classification.

3. The third method used is to separate the MgO from dolomite ($MgCa(CO_3)_2$). It is much easier to dead burn MgO than CaO since CaO has a greater tendency to combine with water and slake, hence several methods have been proposed to extract the MgO from dolomite and use it as a refractory.[1]

This separation of MgO from CaO after calcining the dolomite at various temperatures is accomplished in several ways, such as by chemical-treatment, flotation, elutriation, leaching and screening.

There are also methods used where the dolomite is not previously calcined.[2]

The most promising and generally used methods for attempting to dead burn dolomite for brick purposes are those methods listed in section 1 where the finely ground dolomite is calcined together with a flux.

For dead burning dolomite in granular form, method 2 is in general use.

This grain dolomite is used for bottoms of basic open hearth furnaces and patching. Magnesite bricks are used for the foundation of the bottom and granular dolomite or magnesite for the remainder. When the dolomite is burned at the plant it may be mixed with slag and sintered into place in the same way as magnesite. When prepared dolomites are used, this latter step is sometimes unnecessary as they have the proper composition for setting. Analyses of some of these prepared dolomites are as follows:[3]

| | $SiO_2$ | $Fe_2O_3$-$Al_2O_3$ | CaO | MgO | Mn | Ignition loss |
|---|---|---|---|---|---|---|
| Magdolite | 5.77 | 6.12 | 51.05 | 35.05 | n. d.[1] | 0.82 |
| Magnite | 1.35 | 1.52 | 59.70 | 37.77 | n. d. | .50 |
| Madgebrent | 1.84 | 8.17 | 56.86 | 31.26 | 0.20 | .51 |
| Dolite | 2.20 | 0.86 | 57.37 | 38.16 | n. d. | .85 |
| Syndolag | 4.66 | 6.18 | 52.80 | 31.76 | 0.98 | .51 |

[1] No determination.

The construction of a furnace bottom requires about 90 tons of grains and 25 tons of ground slag.

When a furnace is operated intermittently, especially with prolonged shut-downs, the use of dolomite in any great thickness is unwise because it will slake to a powder upon exposure to the atmosphere. Even treated dolomites slake rather easily.

[1] R. Scherer, "Der Magnesit," *A. Hartleben's Verlag, Wien u. Leipsig*, **84**, 134, 135 (1908); J. A. Bradburn, "Process of Obtaining Magnesia," U. S. 1,156,662, Oct. 2 (1915); A. M. Mitchell, "Process for Obtaining Magnesium Oxide from Dolomites," U. S 1,273,110, July 16 (1918)

[2] H. Scherer, *ibid.*, p. 134.

[3] H. E. Townsend, Report, *Elec. Fur. Assn.*, **79**, Oct. 6 (1920).

Schurecht[1] made a careful study of the effects of fine grinding and different calcination temperatures on dolomite using the following fluxes: flue dust, iron ore, basic open hearth slag, kaolin and roll scale. The dolomite was ground to 100-mesh and 40-mesh and calcined with the above fluxes at cones 14, 20 and 26, in a Hoskins carbon resistance furnace. The tendency to slake is measured by the tendency the body shows to increase in weight.

The results he obtained may be summarized as follows:

**1. Flue Dust and Dolomite.**—Grinding the dolomite to 100-mesh size before calcination decreased its tendency to slake over that of 8-mesh dolomite. Also, increasing the calcination temperature above cone 14 increased the tendency of the dolomite to slake. Increase of flux in 40-mesh dolomite decreased the tendency to slake up to an addition of 10%. Above 10% flux, the tendency to slake varied with different percentages of flux.

**2. Iron Ore and Dolomite.**—Fine grinding of the raw dolomite decreases the tendency to slake. Increasing the calcination temperature above cone 14 again increases the tendency of the dolomite to take up moisture and carbon dioxide. The increase in flux acts similar to flue dust as given in the foregoing paragraph.

**3. Basic Open Hearth Slag and Dolomite.**—A mixture of 8-mesh dolomite and basic open hearth slag increased in weight much more than a similar mixture with 100-mesh dolomite. Increasing the calcination temperature above cone 14 likewise increases the tendency of the body to increase in weight even to a greater extent than when flue dust and iron ore were used as fluxes. This is attributed to the fact that the lime and silica content of the slag forms unstable compounds with the CaO of the dolomite.

**4. Kaolin and Dolomite.**—As before, fine grinding of the raw dolomite increases the resistance to slaking. Also, an increase in calcination temperature above cone 14 increases the tendency of the calcine to increase in weight. This was more pronounced on the high fired specimens than with the corresponding iron ore and flue dust mixtures. Some of the mixtures made with 5 and 10% kaolin were still sound at the end of $2^1/_2$ years storage at room temperature. This is attributed to the comparatively high silica-alumina content which evidently forms hydraulic compounds with the lime, similar to those in Portland cement. Kaolin proved to be a very effective flux in dead burning dolomite, being much better than high iron fluxes, probably due to the fact that alumina and silica are better fluxes of CaO than iron oxide and hence leave less uncombined lime.

[1] H. G. Schurecht, *op. cit.*, **4** [2], 127 (1921).

**5. Roll Scale and Dolomite.**—A mixture of 8-mesh dolomite and roll scale when calcined, increased in weight more than a mixture of 100-mesh dolomite and roll scale, as in the other cases cited. However, increasing the calcination temperature did not materially cause the product to increase in weight.

**6. Chlorides and Dolomite.**—Adding calcium chloride, magnesium chloride and sodium chloride individually to dolomite and calcining, decreased the tendency of the calcine to slake to only a very slight extent.

From the above combinations, the following conclusions are drawn:

(1) Grinding the raw material fine, *i. e.*, through a 100-mesh sieve, seems necessary to produce the best results.

(2) In most cases increasing the calcination temperature above cone 14 increases the tendency of the calcined dolomite mixtures to take up moisture and carbon dioxide and to disintegrate, due to the formation of free lime and hydraulic compounds which hydrate slowly in the open air.

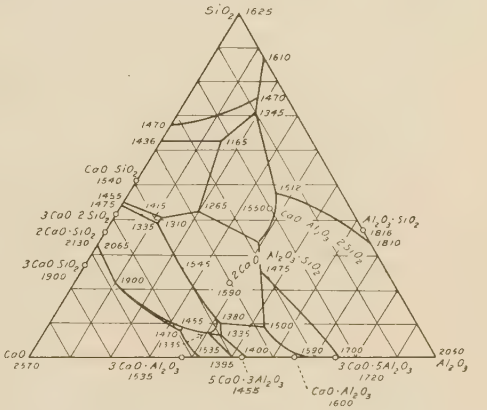



FIG. 1.—Ternary system $CaO–Al_2O_3–SiO_2$.

(3) Kaolin proved to be the most effective flux used for dead-burning dolomite.

### Pyrochemical Behavior of Impurities Found in Dolomite

A review of the work carried on by the Geophysical Laboratory of Washington gives an idea of the pyrochemical behavior of the chief impurities found in dolomites.

The $CaO–Al_2O_3–SiO_2$ diagram as reported by G. A. Rankin,[1] is shown in Fig. 1. Here we have the compounds, $CaOSiO_2$, $3CaO2SiO_2$, $2CaOSiO_2$, $3CaOSiO_2$, $3CaOAl_2O_3$, $5CaO3Al_2O_3$, $CaOAl_2O_3$, $3CaO5Al_2O_3$ and $Al_2O_3$-$SiO_2$. These compounds are at a maximum temperature with eutectics at the points shown. The boundary curves limiting the fields for the stable existence of the compounds (monovariant systems) are also shown. The figures on the diagram denote the fusion points of these mixtures and compounds. Among the natural minerals are found the ternary compounds: anorthite, meionite, gehlenite and grossularite, all lime-silica-alumina minerals. Grossularite and meionite do not form by directly fusing together the pure oxides, but nevertheless exist in the natural

[1] G. A. Rankin, *Am. J. Sci.*, **39**, 25 (1915).

minerals. By fusing together the three oxides CaO, $Al_2O_3$ and $SiO_2$, we may thus obtain, at least, two ternary compounds: anorthite ($CaOAl_2O_3$-$2SiO_2$) and gehlenite ($2CaOAl_2O_3SiO_2$) and the eight binary compounds shown on the diagram.

These compounds are all stable and hence if the free lime ordinarily formed when calcining dolomite can be put into combination as any of these forms, there will be little danger of the hydration of free lime. The chief undesirable constituent to avoid is the $\beta$ orthosilicate which inverts into the stable fine powder $\gamma$ orthosilicate as will be mentioned later. The $\beta$ dicalcium silicate has an index of refraction equal to $1.645 \pm 0.003$, the index of $\gamma$ dicalcium silicate is $1.654 \pm 0.003$. The birefringence is medium, about 0.015.

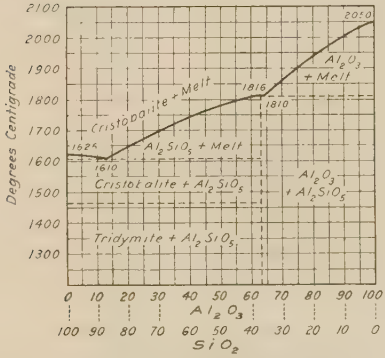



FIG. 2.—Binary system $Al_2O_3$-$SiO_2$. Weight, per cent.

The effect of alumina on silica is shown in Fig. 2. There is only one compound sillimanite, $Al_2O_3SiO_2$, which forms eutectics on either side of it. The eutectic between sillimanite and corundum occurs at 64% $Al_2O_3$ and 36% $SiO_2$ at a temperature slightly below the melting point of pure sillimanite, 1816°C. The eutectic between sillimanite and cristobalite occurs at 1610°C.

## The Ternary System $MgO$–$Al_2O_3$–$SiO_2$[1]

This system is shown in Fig. 3. Here we see that the binary compounds $2MgOSiO_2$ (forsterite), $MgOSiO_2$ (enstatite), $MgOAl_2O_3$ (spinel), $Al_2O_3SiO_2$ (sillimanite), and a ternary compound $2MgO2Al_2O_35SiO_2$ (cordierite) may form, which all have lower melting points than MgO itself besides various eutectics as shown in the triaxial.

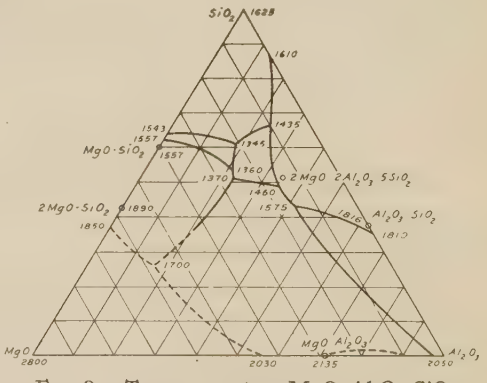



FIG. 3.—Ternary system $MgO$–$Al_2O_3$-$SiO_2$

## The Ternary System $CaO$–$MgO$–$SiO_2$[2]

For this system see Fig. 4. Here the definite compounds $\alpha$ $CaOSiO_2$ (pseudowollastonite), $3CaO2SiO_2$, $\alpha$ and $\beta$ $2CaOSiO_2$, $MgOSiO_2$ (clinoen-

[1] Rankin & Merwin, *Am. J. Sci.*, **45**, 304 (1918).

[2] Ferguson & Merwin, *ibid.*, **48**, 109 (1919).

statite), $2MgOSiO_2$ (forsterite), $CaOMgO2SiO_2$ (diopside), $5CaO2MgO\text{-}6SiO_2$ and $2CaOMgO2SiO_2$ (akermanite) have fusion temperatures as shown on the diagram.

### The System Anorthite–Forsterite–Silica[1]

This system is shown in Fig. 5. The general character of the true ternary part of the diagram is that of a system with no ternary compound and one binary compound, clinoenstatite $MgOSiO_2$ unstable at its melting point of 1557°C. There are two quintuple points. M is an alteration point between anorthite, forsterite and enstatite with a composition of $SiO_2$ 54.20%, $Al_2O_3$ 20.16%, MgO 14.59%, CaO 11.05% and with a melting point of 1260° ± 2°C. The ternary eutectic between anorthite and clinoenstatite and tridymite has a composition of $SiO_2$ 61.90%, $Al_2O_3$ 18.51%, CaO 10.15%, MgO 9.44% having a temperature of 1222° ± 2°C.

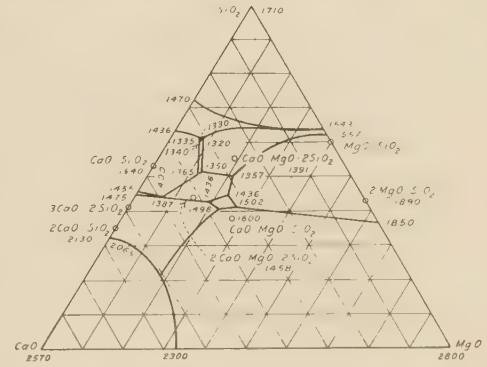



FIG. 4.—Ternary system CaO–MgO–$SiO_2$.

### The Ternary System CaO–$Al_2O_3$–MgO.[2]

This system is shown in Fig. 6. As shown there is no ternary compound formed. There are six quintuple points of the following compositions and melting points:

| Point | | | | Melting point |
|---|---|---|---|---|
| 1 | CaO 51.5 | $Al_2O_3$ 42.3 | MgO 6.2 | 1450° ± 5° |
| 2 | CaO 46.0 | $Al_2O_3$ 47.7 | MgO 6.3 | 1345° ± 5° |
| 3 | CaO 41.5 | $Al_2O_3$ 51.8 | MgO 6.7 | 1345° ± 5° |
| 4 | CaO 40.7 | $Al_2O_3$ 52.4 | MgO 6.9 | 1370° ± 5° |
| 5 | CaO 33.3 | $Al_2O_3$ 63.2 | MgO 3.5 | 1550° ± 5° |
| 6 | CaO 21.0 | $Al_2O_3$ 74.0 | MgO 5.0 | 1680° ± 20° |

### Preliminary Report on the System Lime–Ferric Oxide[3]

Figure 7 shows the binary system lime–ferric oxide. There are only two calcium ferrites having the formula of the dicalcic ferrite ($2CaOFe_2O_3$) and the monocalcic ferrite ($CaOFe_2O_3$) with dissociation temperatures at 1436° and 1216°C, respectively.

[1] Olaf Anderson, *Am. J. Sci.*, **39**, 440 (1915).
[2] Rankin & Merwin, *J. Am. Chem. Soc.*, **38**, 575 (1916).
[3] Sosman and Merwin, *J. Wash. Acad. Sci.*, **6**, 532–7 (1916).

Campbell[1] shows that if a mixture of pure silica, ferric oxide and calcium oxide of the same molecular proportion as those found in the celite drawn off from Portland cement clinker, is melted and slowly cooled, large crystals of tricalcic silicate will separate, thus demonstrating that calcium ferrite may act as a solvent for both calcium silicate and lime, in a manner almost exactly similar to that of the calcium aluminate.[2]

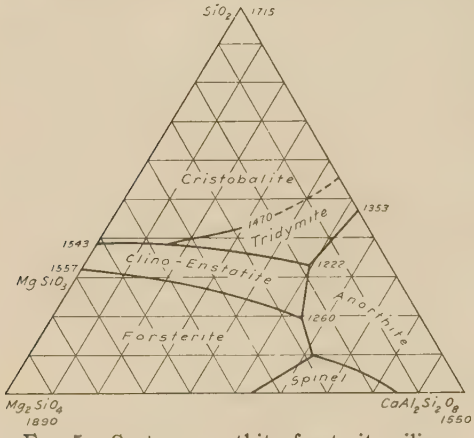



FIG. 5.—System anorthite–forsterite–silica.

### CaO–MgO System[3]

Figure 8 shows the effect of lowering the melting point of MgO by the presence of CaO. In this system it was found that in all fused mixtures of CaO and MgO, the two oxides crystallize out side by side, showing no evidence of combination, that is, there is no stable compound formed. The eutectic formed has the approximate composition CaO 67%, MgO 33% and its melting point is 2300° ± 50° which, as seen from the other curves shown, is a higher fusion point than where $Al_2O_3$, $Fe_2O_3$ or $SiO_2$ are added to CaO or MgO.

The effect of $Al_2O_3$ and $SiO_2$ on lowering the fusion temperature of CaO, MgO and CaO MgO (the theoretical ratio in which CaO and MgO exist in dolomite), as obtained from the previous curves is shown in Figs. 9 and 10. These curves show that $SiO_2$ has a much greater effect on lowering the fusion temperature of MgO than $Al_2O_3$ has.

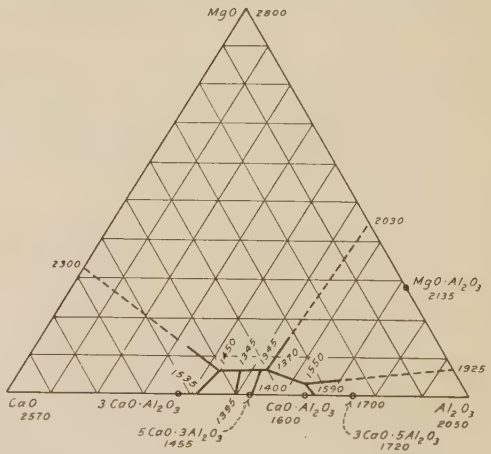



FIG. 6.—Ternary system CaO–$Al_2O_3$–MgO.

$SiO_2$ lowers the fusion temperature of CaO

[1] Campbell, "Function of Ferric Oxide in the Formation of Portland Cement Clinker," *J. Ind. Eng. Chem.*, **7**, 835–7 (1915).

[2] H. A. Miers, *Mineralogy*, p. 385 (1902) states that iron oxide forms a spinel with $Al_2O_3$ of the formula $FeOAl_2O_3$ called hercynite.

[3] Rankin and Merwin, *J Am. Chem. Soc.*, **38**, 571 (1916)

MgO more rapidly and to a lower temperature than does $Al_2O_3$. On the contrary $Al_2O_3$ lowers the fusion temperature of CaO more rapidly and to a greater extent than does $SiO_2$. The fusion temperature of CaO MgO with $SiO_2$ as a flux is lower than that of CaO or MgO alone with $SiO_2$ as a flux. In greater amounts than about 21% and less than about 83%, $Al_2O_3$ lowers the fusion temperature of pure CaO below that of CaO MgO.

Schurecht[1] found that a large percentage of iron oxide 20–30% with 80–70% dolomite may be used without decreasing the refractoriness below cone 31. Impurities which are siliceous in character like kaolin, he found to decrease the refractoriness to a much greater extent. Work later on in this article will show that it was probably not the presence of silica which caused the decrease in refractoriness, but the presence of $Al_2O_3$ which caused the excessive lowering in the fusion temperature.

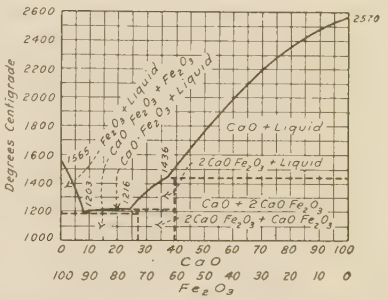



FIG. 7.—The binary system CaO–$Fe_2O_3$.

From these aforementioned diagrams and data we see that any of the following compounds may exist in dead-burned dolomite when $Fe_2O_3$, $Al_2O_3$ and $SiO_2$ are present:

| | |
|---|---|
| CaO $SiO_2$—Wollastonite | $3CaO\ 5Al_2O_3$ |
| $3CaO\ 2SiO_2$ | CaO $Al_2O_3$ $2SiO_2$—Anorthite |
| $2CaO\ SiO_2$—Calcium orthosilicate | $2CaO\ Al_2O_3\ SiO_2$—Gehlenite |
| $3CaO\ SiO_2$—Tricalcium silicate | MgO $SiO_2$—Enstatite |
| CaO MgO $SiO_2$—Monticellite | $2MgO\ SiO_2$—Forsterite |
| CaO MgO $2SiO_2$—Diopside | MgO $Al_2O_3$—Spinel |
| $2CaO\ MgO\ 2SiO_2$—Akermanite | $2MgO\ 2Al_2O_3\ 5SiO_2$—Cordierite |
| $5CaO\ 2MgO\ 6SiO_2$ | $5CaO\ 2MgO\ 6SiO_2$ |
| $3CaO\ Al_2O_3$—Tricalcium aluminate | $Al_2O_3\ SiO_2$—Sillimanite |
| $5CaO\ 3Al_2O_3$ | $2CaO\ Fe_2O_3$—Dicalcic ferrite |
| CaO $Al_2O_3$—Calcium aluminate | CaO $Fe_2O_3$—Monocalcic ferrite |

Since, as shown by these diagrams, the compounds and especially the eutectic mixtures have fusion points at relatively low temperatures, in all probability the amount of flux added to the dolomite will have to be limited to within a few per cent of the dolomite so as not to exercise too great an influence on the softening temperature of the mixture, thus destroying its value as a refractory.

Of course these diagrams represent equilibrium conditions, *i. e.*, that the compounds and components as represented would occur together in mixtures if time were allowed for the reaction to go to completion which most

[1] H. G. Schurecht, *J. Am. Ceram. Soc.*, **2** [4], 305 (1919).

probably will not be the actual case when dolomite is calcined with fluxes. The diagrams show, however, what compounds may be formed in calcining such a mixture. They show that there are numerous possibilities in forming various eutectic mixtures and also stable compounds which may be formed by reaction of the fluxing oxides with CaO and MgO of the dolomite, or it is possible that a eutectic mixture or compound may be formed between all the oxides which will dissolve the excess CaO and MgO, thus producing a stable form. Absolutely dead-burned magnesite has the magnesite essentially in the form of periclase.[1] By adding fluxes to dolomite and calcining at a sufficiently high temperature, it may be possible to form the MgO into periclase and have the otherwise free lime, which would tend to slake, combine with the fluxes present to form stable compounds.

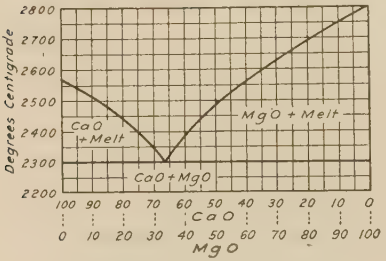



FIG. 8.—Binary system CaO–MgO.

Austrian magnesite, which dead burns to form the ordinary magnesia brick, is called Breunnerite, which is an isomorphous mixture of magnesium and iron carbonates. When this mineral is calcined and dead burned the resulting product takes on a yellowish tinge. This is due to the solution of the ferric oxide formed into the periclase formed. Adding iron oxide to a magnesite too low in the iron oxide content gives a satisfactory product.[2]

The composition of Breunnerite varies from 95–70% $MgCO_3$ and 5–30% $FeCO_3$.[3]

Pike[4] states that amorphous magnesite raised to a temperature of 1550°C in the presence of 5–6% $Fe_2O_3$ is transformed into periclase which is dense, hard and sintered and known as dead-burned magnesite. Microscopic examination demonstrates that $Fe_2O_3$ added to the rock under proper conditions is equivalent in action to the iron occurring naturally in the rock. The natural occurring

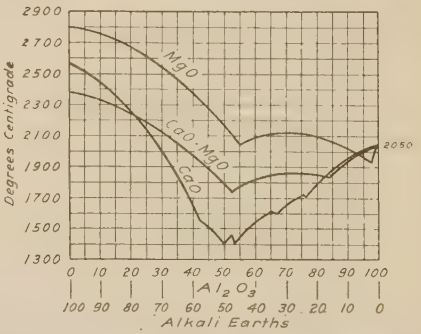



FIG. 9.—Effect of $Al_2O_3$ on the fusion o f CaO, MgO and CaO. MgO.

[1] J. S. McDowell and R. M. Howe, "Magnesite Refractories," *J. Am. Ceram. Soc.*, **3** [3], 211 (1920).

[2] J. S. McDowell and R. M. Howe, *loc. cit.*, **3** [3], 190–1 (1920).

[3] Thos. Crook, "Magnesite as Raw Material," *Trans. Ceram. Soc.* (Eng.), **18**, 75 (1918–19).

[4] R. D. Pike, "Electric Furnace Refractories," *Chem. Met. Eng.*, **23**, 1148 (1920).

crystalline Austrian magnesite or Breunnerite, however, is far superior to other forms of magnesite[1] and is the chief product used for making magnesia brick in the United States today. Since Breunnerite which contains iron carbonate, forms a better dead-burned product than crystalline Washington magnesite which is low in iron, and since a small percentage of iron oxide, 4.5–8.0%, is considered necessary for the production of dead-burned magnesite for refractory purposes,[2] it appears to be advisable to add it as one of the fluxes in dead-burning dolomite, since if a small percentage of ferric oxide is added to a pure dolomite, the two finely ground together and calcined at a high temperature, there is a tendency to approach the homogeneous composition of Breunnerite.

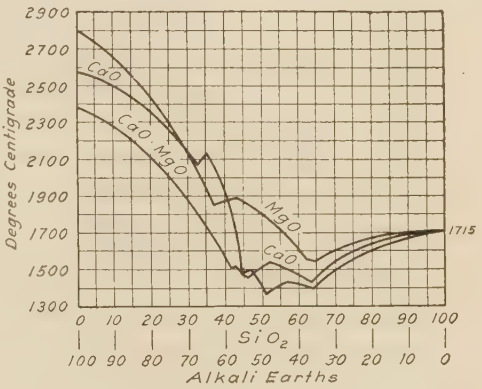



FIG. 10.—Effect of $SiO_2$ on the fusion of CaO, MgO and CaO . MgO.

The presence of impurities, especially silica and silicates, causes lime to be overburned. This appears to be true since it has been found practically impossible to overburn some very pure limes.[3] Overburned lime is generally yellow or black in color. It is very inactive to water and slakes not at all or very slowly. Thus the presence of silica or silicates when mixed with dolomite may tend to cause the lime to "overburn" when calcined.

## Slaking of Dolomite

The disintegration of dolomite is due to the two following causes:

1. Disintegration due to change of state on heating and cooling.
2. Disintegration due to slaking by taking up moisture from the air.

In the first case the disintegration is comparatively rapid occurring during the cooling and is due to the inversion from the $\beta$ to $\gamma$ form of orthosilicate which starts at about 675°C[4] and continues even after it is removed from the furnace. This inversion is accompanied by a 10% volume change which causes dusting of the orthosilicate and the dolomite

[1] A. F. Greaves-Walker, "Electric Furnace Refractories," *Elec. Fur. Assn.*, **57**, Oct. 6 (1920).

[2] McDowell and Howe, *loc. cit.*, **3** [3], 203 (1920).

[3] W. E. Emley, U. S. Bur. Stand., *Tech. Paper* **16** (1913).

[4] Shepard and Rankin, "Preliminary Report on the Ternary System $CaO–Al_2O_3–SiO_2$," *J. Ind. Eng. Chem.*, **3**, 9 (1911).

containing it. Newberry, Richardson, Boudouard and Le Chatelier[1] all noticed this dusting and Le Chatelier ascribed it properly as being due to polymorphism. Schurecht[2] found that blast furnace slag used as a flux for dolomite caused considerable dusting due to this conversion of $\beta$ $2CaOSiO_2$ to $\gamma$ $2CaOSiO_2$. This was caused by the high $SiO_2$ content of the flux. He noticed this dusting to a less extent when flue dust, kaolin or basic open hearth slag were used and mixtures containing roll scale or iron ore showed the least dusting as would be expected. Bates[3] showed that in Portland cement containing above 4.5% MgO, the rapidity and amount of dusting increases with the magnesia content up to about 9.5% MgO content when the orthosilicate begins to decrease again with addition of MgO.

Disintegration due to taking up moisture from the air is due primarily to the presence of free lime in the calcined material which takes up water and forms calcium hydroxide according to the simple chemical equation

$$CaO + HOH \longrightarrow Ca(OH)_2.$$

This is purely a case of lime slaking where the increased volume of the $Ca(OH)_2$ disrupts the mass causing it to slake down into powder. As a secondary reaction we have

$$Ca(OH)_2 + CO_2 \longrightarrow CaCO_3 + H_2O.$$

Davis[4] shows that "underburned" cement contains a considerable quantity of free lime. Cements such as this when mixed with water set rapidly. The particles of free lime absorb moisture changing to the hydrate of lime and the expansion which accompanies this change produces ominous cracks in the hardened cement.

This disintegration, due to the taking up of moisture, may also be due to various compounds formed in the calcine which possess hydraulic properties and in taking up water from the air, cause the calcined material to disintegrate. Klein and Phillips[5] found that the following compounds will hydrate: $3CaO\ Al_2O_3$, $5CaO\ 3Al_2O_3$, $CaO\ Al_2O_3$, $3CaO\ SiO_2$ and $\beta$ $2\ CaO\text{-}SiO_2$. They found that $CaO\ SiO_2$ and $\gamma$ $2CaO\ SiO_2$ do not possess hydraulic properties. Campbell[6] showed that the two ferrites of calcium, monocalcic ferrite and dicalcic ferrite will hydrate also. Magnesium oxide will

[1] Newberry, *J. Soc. Chem. Ind.*, **16,** 887 (1897); Richardson, *Cement,* **4,** 276 (1903); Boudouard, *Rev. de Metal,* 462 (1905); LeChatelier, *Ann. d. Mines,* 345 (1887).

[2] H. G. Schurecht, *J. Am. Ceram. Soc.*, **2** [4], 304 (1919).

[3] P. H. Bates, "Properties of Portland Cement having a High Magnesia Content," U. S. Bur. Stand., *Tech. Paper* **102,** 40 (1918).

[4] A. C. Davis, *Port. Cement,* **22** (1909).

[5] Klein and Phillips, "The Hydration of Portland Cement," *Trans. Am. Ceram. Soc.*, **16,** 313–41 (1914).

[6] E. D. Campbell, *J. Ind. Eng. Chem.*, **11,** 116–20 (1919).

combine with water with reasonable rapidity, only when it has been burned at some temperature below 1100°C. It may be that these compounds, if present in sintered dolomite, will, during the process of their hydration, cause a volume change and cause the calcined dolomite to disintegrate. Schurecht's work showed that compounds having a tendency to increase in weight when exposed to the air are formed in dolomite calcined with various fluxes. Bates[1] shows that Portland cement high in magnesia produces concrete similar, so far as expansion is concerned, to concrete made from the normal composition. This cement shows usually contraction when stored in air and expansion when stored in water. The expansion and contraction of these compounds, however, is only very slight, in most cases not more than a few hundredths of one per cent. A large part of the magnesium does not hydrate, it acts merely as an inert substance which must be heated by the calcium oxide. Therefore, other things being equal, the less magnesium oxide present in a lime, the more quickly will it slake and the greater will be the amount of heat generated. However, a very porous dolomitic lime may slake more quickly than a dense lime with a much higher content of calcium oxide, due to the fact that the water can penetrate the more porous lime more quickly. Evidently it appears that in order to dead burn dolomite, a dolomite of as high MgO content as possible is desirable and as previously mentioned, a fine grained material is desirable in order to develop a dense product.

## Summary

Thus it has been shown that:

1. Kaolin appears to be a fairly effective flux for dead-burning dolomite.
2. There are many different compounds and eutectic mixtures capable of formation among the five components CaO, MgO, $Fe_2O_3$, $Al_2O_3$, and $SiO_2$.
3. CaO may combine with $Fe_2O_3$ and act as a solvent for lime as does also calcium aluminate.
4. The presence of $Fe_2O_3$ is essential to dead burn MgO to the stable form periclase.
5. Lime is rendered inactive to water by calcination in the presence of impurities especially silica and silicates.
6. The more magnesium oxide present in a lime, the slower will it slake.

In view of these facts it was deemed advisable to carry on this investigation of determining whether or not it is possible to dead burn dolomite using $Fe_2O_3$, $Al_2O_3$ and $SiO_2$ either alone, a combination of any two, or a combination of all three as fluxes.

[1] P. H. Bates, *op. cit.*, 21–4.

## Preliminary Investigation

There are many large deposits of dolomite in the United States. These range from the very pure dolomite of Ohio and the eastern states, notably New York and Pennsylvania which correspond very closely to the theoretical formula $CaCO_3$ $MgCO_3$ to dolomites which are very low in MgO content.

Throughout this work, a pure variety of dolomite obtained from the Niagara deposit at Cedarville, Ohio, was used.

It analyzed as follows:

| | | | |
|---|---|---|---|
| Silica ($SiO_2$)..... | 0.4 | Potassium oxide ($K_2O$)... | trace |
| Aluminum oxide ($Al_2O_3$).. | 0.5 | Sodium oxide ($Na_2O$)..... | trace |
| Ferric oxide ($Fe_2O_3$)..... | 0.5 | Sulfur trioxide ($SO_3$)..... | none |
| Calcium oxide (CaO).... | 30.2 | Carbon dioxide ($CO_2$).... | 46.8 |
| Magnesium oxide (MgO). | 21.8 | | 100.2 |

The true specific gravity of this dolomite is 2.85.

This dolomite was crushed in jaw crushers, then ground through rolls and finally ground in the dry pan until it all passed 100 mesh, which Schurecht[1] found to be the best degree of fineness. After the entire batch had been screened, it was again thoroughly mixed for about 15 minutes in a dry pan so that the harder material was evenly distributed throughout the softer material which passed through the screen first.

## Series 1A

The pulverized dolomite was then mixed with $Al_2O_3$, $Fe_2O_3$ and $SiO_2$ in the proportion of 90% dolomite by weight to 10% of flux by weight maintaining the 90% of dolomite constant and blending the 10% of fluxes in a three variable series consisting of twenty-two members apportioned as follows:

| Number | $Fe_2O_3$ | $Al_2O_3$ | $SiO_2$ | Number | $Fe_2O_3$ | $Al_2O_3$ | $SiO_2$ |
|---|---|---|---|---|---|---|---|
| 1A1 | 10 | .. | .. | 12 | 2 | 8 | .. |
| 2 | 8 | 2 | .. | 13 | 2 | 6 | 2 |
| 3 | 8 | .. | 2 | 14 | 2 | 4 | 4 |
| 4 | 6 | 4 | .. | 15 | 2 | 2 | 6 |
| 5 | 6 | 2 | 2 | 16 | 2 | .. | 8 |
| 6 | 6 | .. | 4 | 17 | .. | 10 | .. |
| 7 | 4 | 6 | .. | 18 | .. | 8 | 2 |
| 8 | 4 | 4 | 2 | 19 | .. | 6 | 4 |
| 9 | 4 | 2 | 4 | 20 | .. | 4 | 6 |
| 10 | 4 | .. | 6 | 21 | .. | 2 | 8 |
| 11 | 3.33 | 3.33 | 3.33 | 22 | .. | .. | 10 |

[1] *Jour. Amer. Ceram. Soc.*, **4** [2], 133(1921).

J. T. Baker's analyzed alumina and ferric oxide, also flint obtained from the Pennsylvania Pulverizing Co., were used as fluxes. These analyzed as follows:

| Alumina | | Ferric oxide | | Flint | |
|---|---|---|---|---|---|
| $Al_2O_3$..... | 99.99% | $Fe_2O_3$..... | 99.99% | $SiO_2$..... | 99.81% |
| $SiO_2$..... | 0.001% | FeO..... | trace | $Al_2O_3$..... | 0.17% |
| Fe..... | .005% | $SO_3$..... | 0.007% | $Fe_2O_3$..... | 0.014% |
| CaO..... | .001% | | | CaO..... | none |
| Cl..... | .001% | | | MgO..... | none |
| $SO_3$..... | .001% | | | | |

These analyses were made on the samples after drying at 105°C. The amount of moisture present in each was as follows:

| Alumina | Ferric oxide | Flint | Dolomite |
|---|---|---|---|
| 0.24% | 0.32% | 0.07% | 0.11% |

## Moisture

In all compositions, corrections were made for moisture, *e. g.*, a 3200 gram batch of member 1A calls for 2880 grams of dolomite (=90%) and 320 grams of iron oxide (=10%). The amount of moisture in the dolomite is 0.11%, therefore $\frac{2880}{(100-0.11)} \times 100 = 2883.2$ grams of dolomite required. The moisture in the iron ore is 0.32%, hence $320 \div (100-0.32) \times 100 = 321.03$ grams of iron ore were added to 2883.2 grams of dolomite giving a 90% dolomite and 10% ferric oxide mixture.

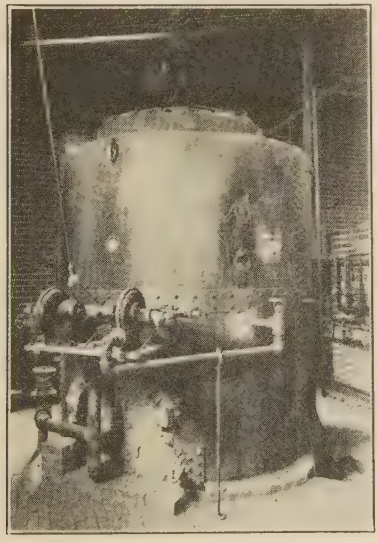


Fig. 11.—Gas fired kiln.

The end members 1A1, 1A17 and 1A22 were prepared by grinding the dolomite with the respective oxides in the dry pan for about one hour or until the added flux was thoroughly mixed throughout the dolomite as shown by a very uniform color. These end members were then blended, so as to produce the intermediate members by weighing out the proper quantity of each.

Thoroughly mixing with a spatula, rolling back and forth on paper and screening through a 40-mesh screen twice. After this mixing which required about 20 minutes for each member of 400 grams, the blends were uniform in composition as shown by the uniformity of color in members where iron oxide was used.

One-inch cubes of the various mixtures were made by tempering the mix with water until it molded well. The average amount of water required was about 20% on the dry weight basis. The dry cubes were burned in a down-draft gas fired furnace shown in Fig. 11, to cone 16 down. The time for the burn was 54 hours. The temperature of burning as recorded by the pyrometer at 2-hour intervals is shown in Fig. 12. The curve is given to show the approximate rate of burning. Cones were placed throughout the kiln and all plaques of cones after the burn showed the heat to be evenly distributed throughout, that is, cone 16 down.

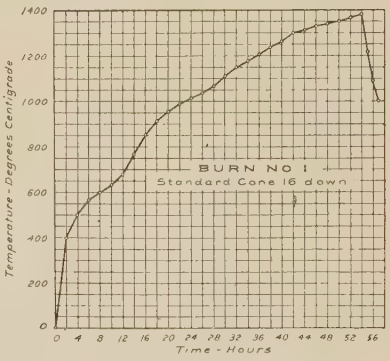



FIG. 12.

## Burning Results of Series 1A

The colors of the burned cubes varied from black in the high iron oxide field to light brown in the alumina field to a pale green in the silica field. These colors are to be expected, the black due to the iron, the brown due to the alumina as in Portland cement clinker and the green similar to an ordinary lime silica slag. For colors of each member, see the following (Table I).

TABLE I

COLOR OF BURNED CUBES

| Series 1A | | Series B | |
|---|---|---|---|
| Member | Color | Member | Color |
| 1–15 | Black | 1–16 | Black |
| 16 | Dark brown | 17 | Brown |
| 17 | Light brown | 18 | Brownish green |
| 18 | Greenish brown | 19–23 | Green |
| 19 | Pale green | 24 | Yellowish green |
| 20–21 | Bluish green | | |
| 22 | Yellowish green | | |

These cubes were set in the kiln on chrome powder spread over silica brick, to prevent fluxing between the dolomite and silica. Cubes of each member were also placed in the kiln on silica brick alone. Because of their strongly basic action, the cubes in contact with the silica fluxed partially down into the brick. Members 5, 6, 19 and 21 dusted down completely in the kiln when supported on silica brick. This was due to the formation of calcium orthosilicate and its consequent inversion from the beta to the gamma form as previously described in the introduction. This presence of the orthosilicate was confirmed by examination of some of the dust under the microscope. No cubes which were set on powdered chrome

completely disintegrated in the kiln; however, there was slight dusting on the bottom of all the cubes when they came in contact with the ore.

After removing the cubes from the kiln, the following properties were tested on separate cubes:

1. Air slaking resistance at room temperature.—Determined by allowing the cubes to stand in the laboratory and noting once per week the time at which they started to disintegrate or dust down.

2. Outside air slaking resistance.—Determined by allowing the cubes to stand outside on the window sill and noting when disintegration started.

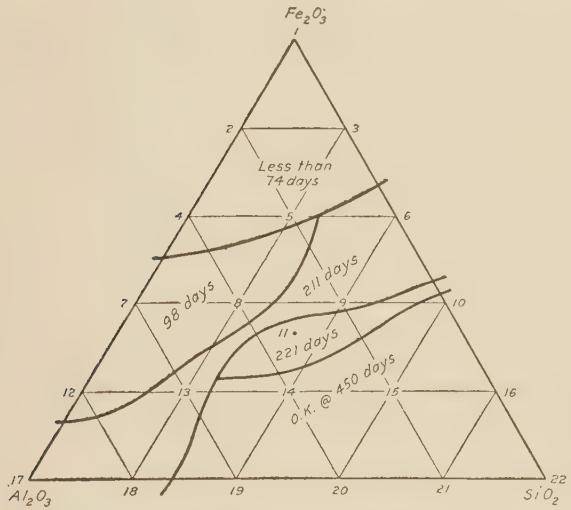



Fig. 13.—Room temperature air slaking test of series 1A.

3. Hot water test.—Cubes were placed in a pan of water and placed on the hot plate. The temperature of the water varied from 70–80°C. The water was renewed each day. Several times, due to fluctuation in the gas pressure, the water in the pan evaporated over night. In this case, without allowing the pan and its contents to cool, water directly from the faucet was run in on the hot cubes and the pan again placed on the hot plate.

## Results of Tests on Series 1A

**Room Temperature Air Slaking Test.**—The results of the room temperature air slaking test are given in Table II and shown on Fig. 13. Here it is seen that the mixtures high in iron oxide are the least stable,

Table II

Series 1A

Air slaking test at room temperature

| Cube no. | No. of days exposed before disintegrating | Order of slaking |
|---|---|---|
| 1–5 | 71–73 | First |
| 7, 8 and 12 | 98 | Second |
| 6, 9, 13, 17 and 18 | 211 | Third |
| 11 | 221 | Fourth |
| 10. 14. 15. 16. 19. 20. 21. 22 | Not slaked after 450 days' exposure | Fifth |

TABLE II—(*Continued*)

SERIES 1A

Outside air slaking test

| Cube no. | No. of days exposed before disintegrating | Order of slaking |
|---|---|---|
| 1, 2 and 4 | 50 | First |
| 3 | 71 | Second |
| 5 | 92 | Third |
| 7, 8 and 12 | 106 | Fourth |
| 13, 17 and 18 | 149 | Fifth |
| 9 and 16 | 223 | Sixth |
| 6, 10, 11, 14, 15, 19, 20, 21, 22 | Not slaked after 450 days' exposure | |

Hot water slaking test

| Cube no. | No. of days soaked before disintegrating | Order of slaking |
|---|---|---|
| 1, 2, 3, 4, 5, 7, 8, 12 and 17 | 1 | First |
| 13 and 18 | 2 | Second |
| 16, 19, 21 and 22 | 5 | Third |
| 6 and 10 | 18 | Fourth |
| 9, 11, 15 and 20 | 50 | Fifth |
| 14 | 99 | Sixth |

whereas coming down toward the silica field, members 14, 15, 16, 19, 20, 21, and 22 have not yet disintegrated after 450 days' exposure, showing them to be very stable at room temperature when protected from the weather, so that it appears as though silica, 10% or less, stabilizes calcined dolomite with regard to slaking in the air.

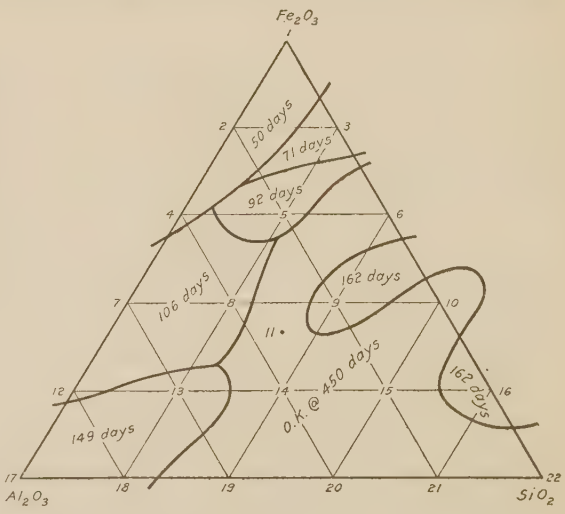



FIG. 14.—Outside air slaking test of series 1A.

**Outside Air Slaking Test.**—The results of this test shown in Table II and Fig. 14, follow somewhat according to the order of those obtained in the room temperature air slaking test, more accelerated in some cases and slower in others. Here again in general, the high iron region slaked down first, the high alumina region next. The middle region and that of the silica field are the most stable. As shown, these stable compositions have not slaked after 450 days' exposure in the air.

After about two weeks' exposure, all cubes were covered in places with a

white coating which upon analysis proved to be $CaCO_3$. This lime was no doubt due to free lime present in the cube combining with $CO_2$ from the air.

Two cubes of each member were tested here and in all cases those of the same composition disintegrated at the same time.

As mentioned, this test does not appear to be much different from the inside slaking test.

**Hot Water Slaking Test.**—For results of this test see Table II and Fig. 15. Here again, the region high in iron is the most unstable together with the members highest in alumina. In general, the field high in $Al_2O_3$ is more unstable than that in the silica field. However, the most stable field appears to be near the middle of the diagram, where all three oxides are present.

By far, the most stable composition in this series is member 1A14, whose composition is as follows:

| | |
|---|---|
| Dolomite | 90.0% |
| $Fe_2O_3$ | 2.0 |
| $Al_2O_3$ | 4.0 |
| $SiO_2$ | 4.0 |

This composition gives a formula as follows:

$$\left.\begin{matrix}0.5\ CaO\\0.5\ MgO\end{matrix}\right\}\left\{\begin{matrix}0.0399\ Al_2O_3\\.0128\ Fe_2O_3\end{matrix}\right\}\ 0.0685\ SiO_2.$$

In fact, this body 1A14 did not actually slake down. It simply cracked into three or four pieces after heating in warm water for 99 days. In the immediate field around 1A14 toward the $SiO_2$ corner as shown in Fig. 14, members 1A9, 1A11, 1A15 and 1A20 were the next most stable, withstanding this boiling test for 50 days before breaking down. These members like 1A14 simply cracked into 3 or 4 pieces and did not slake down into a powder as was the case with the more unstable compositions. This cracking may have been due to an expansion and contraction effect, since cold water was occasionally poured on the hot cubes as described in the method of procedure. It is

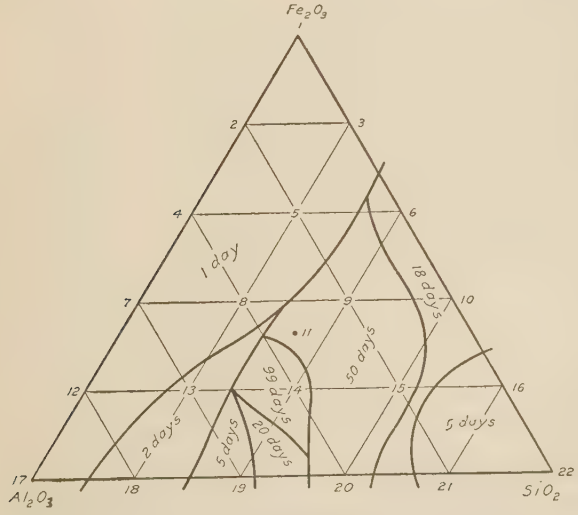



FIG. 15.—Warm water slaking test of series 1A.

thus seen that with this more severe and more accelerated test, the central field again proves to be the most stable, being more stable than the high silica field. In this test a considerable scum of $CaCO_3$ formed on the surface of the water in which the bodies were immersed.

Two cubes of each member were used in this test and again both slaked at the same time.

## Series B

The next preliminary study was made in series B consisting of a twenty-four member series blending 90% of dolomite constant with 10% of variable fluxes blended on the molecular basis. The molecular ratios and corresponding percentage compositions by weight for this series are shown in Table III.

TABLE III

| Member | Molecular ratio | Percentage composition $Fe_2O_3$ | $Al_2O_3$ | $SiO_2$ |
|---|---|---|---|---|
| 1 | $Fe_2O_3$ | 10.0 | ... | ... |
| 2 | $.8Fe_2O_3$ $.2Al_2O_3$ | 8.625 | 1.375 | ... |
| 3 | $.8Fe_2O_3$ $.2SiO_2$ | 9.140 | ... | 0.860 |
| 4 | $.6Fe_2O_3$ $.4Al_2O_3$ | 7.010 | 2.990 | ... |
| 5 | $.6Fe_2O_3$ $.2Al_2O_3$ $.2SiO_2$ | 7.475 | 1.590 | 0.935 |
| 6 | $.6Fe_2O_3$ $.4SiO_2$ | 8.000 | ... | 2.000 |
| 7 | $.4Fe_2O_3$ $.6Al_2O_3$ | 4.730 | 5.270 | ... |
| 8 | $.4Fe_2O_3$ $.4Al_2O_3$ $.2SiO_2$ | 5.480 | 3.500 | 1.020 |
| 9 | $.4Fe_2O_3$ $.2Al\ O_3$ $.4SiO_2$ | 5.900 | 1.885 | 2.215 |
| 10 | $.4Fe_2O_3$ $.6SiO_2$ | 6.400 | ... | 3.600 |
| 11 | $.33Fe_2O_3$ $.33Al_2O_3$ $.33SiO_2$ | 4.965 | 3.165 | 1.865 |
| 12 | $.2Fe_2O_3$ $.8Al_2O_3$ | 2.820 | 7.180 | ... |
| 13 | $.2Fe_2O_3$ $.6Al_2O_3$ $.2SiO_2$ | 3.04 | 5.82 | 1.14 |
| 14 | $.2Fe_2O_3$ $.4Al_2O_3$ $.4SiO_2$ | 3.300 | 4.220 | 2.480 |
| 15 | $.2Fe_2O_3$ $.2Al_2O_3$ $.6SiO_2$ | 3.620 | 2.310 | 4.070 |
| 16 | $.2Fe_2O_3$ $.8SiO_2$ | 4.000 | ... | 6.000 |
| 17 | $Al_2O_3$ | ... | 10.00 | ... |
| 18 | $.8Al_2O_3$ $.2SiO_2$ | ... | 8.720 | 1.280 |
| 19 | $.6Al_2O_3$ $.4SiO_2$ | ... | 7.180 | 2.820 |
| 20 | $Al_2O_3$ $SiO_2$ | ... | 6.300 | 3.700 |
| 21 | $.4Al_2O_3$ $.6SiO_2$ | ... | 5.320 | 4.680 |
| 22 | $Al_2O_3$ $2SiO_2$ | ... | 4.600 | 5.400 |
| 23 | $.2Al_2O_3$ $.8SiO_2$ | ... | 2.980 | 7.020 |
| 24 | $SiO_2$ | ... | ... | 10.00 |

Member B20 contains $Al_2O_3$ and $SiO_2$ in the proportion in which they exist in sillimanite ($Al_2O_3 \cdot SiO_2$), while member B22 contains $Al_2O_3$ and $SiO_2$ in the same proportion as they exist in kaolin. These members were prepared in the same manner as those in series 1A, being made into cubes and burned with series 1A.

The members of this series were all burned on chromite powder. Because of lack of material only 3 cubes of each member were made.

### Color

The cubes in general were the same color as in series 1A, *i. e.*, those containing $Fe_2O_3$ were black, $Al_2O_3$ gave a pale brown color and $SiO_2$ gave a green color. For colors of each member see Table I.

### Results of Tests on Series B

**Inside Air Slaking Test.**—But one cube of each member was exposed to this test. The results are given in Table IV and Fig. 16. Here it is seen as likewise in series 1A, the unstable field is again toward that high in iron and the stable field toward the silica end of the diagram. In this series the very unstable iron field includes two more members, B4 and B6, than series 1A. However, the general slaking fields are very close to being the same, the more stable field again, being down toward the high silica region. Eight of the members as shown, are still stable after 450 days' exposure. It is noticeable that members 1A and B series, which have the same or nearly the same percentage composition by weight, also agree very closely in their air slaking resistance. These members are 1A3 and B6; 1A6 and B10; 1A10 and B16; 1A19 and B20. For example, 1A3 containing 8% $Fe_2O_3$ and 2% $SiO_2$ and B6 containing the same percentage of oxide both slaked after about 71 days exposure; 1A6 containing 6% $Fe_2O_3$ and 4% $SiO_2$ and B10 containing 6.4% $Fe_2O_3$ and 3.6% $SiO_2$ slaked after 211 days and 220 days, respectively. 1A10 and B16 having the same composition are still stable after 450 days' exposure. 1A19 containing 6.0% $Al_2O_3$ and 4.0% $SiO_2$ and B20 containing 6.3% $Al_2O_3$ and 3.7% $SiO_2$ are still stable after 450 days.

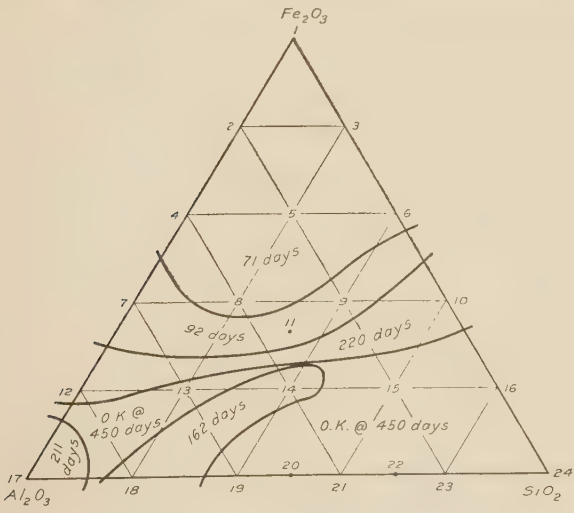



Fig. 16.—Room temperature air slaking test of series B.

Thus it appears that with 10% of flux and 90% of dolomite the percentage composition of the fluxes may be varied slightly among themselves

without making any very noticeable change in the air slaking resistance of the calcined mixture.

TABLE IV

SERIES B

Air slaking test at room temperature

| Cube no. | No. of days exposed before disintegrating | Order of slaking |
|---|---|---|
| 1, 2, 3, 4, 5, 6, 8 | 71 | First |
| 7, 9, 11 | 92 | Second |
| 14, 18 | 162 | Third |
| 17 | 211 | Fourth |
| 10, 12 | 220 | Fifth |
| 13, 15, 16, 19, 20, 21, 22, 23, 24 | Not slaked after 450 days' exposure | |

Hot water slaking test

| Cube no. | No. of days soaked before disintegrating | Order of slaking |
|---|---|---|
| 1, 2, 3, 4, 5, 6, 7, 11, 12 | Less than 1 | First |
| 8, 9, 10, 14, 17, 19, 20 | Less than 2 | Second |
| 18, 24 | 5 | Third |
| 16 | 18 | Fourth |
| 13, 22 | 68 | Fifth |
| 15 | 72 | Sixth |
| 21, 23 | Not slaked after 99 days | |

**Hot Water Slaking Test.**—The results are given in Table IV and Fig. 17. The region high in iron is the most unstable. The region highest in $Al_2O_3$ and that near the middle of the three fields are next, while the most stable members are B21 and B23 whose flux molecular ratios are $.4Al_2O_3.6SiO_2$ and $.2Al_2O_3.8SiO_2$ respectively, neither contains any $Fe_2O_3$. These two members after undergoing the boiling test for 99 days without slaking or cracking were allowed to stand in the air at room temperature for 172 days, then placed in the hot water bath described later and broke down after soaking four days in water at a temperature of 75–85°C.

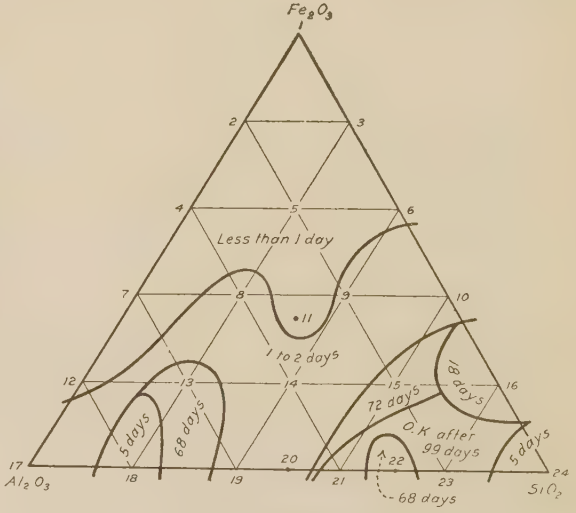



FIG. 17.—Warm water slaking test of series B.

Contrary to the air slaking test, a slight variation in the percentage composition of the fluxes appears to affect the water slaking resistance of the cubes quite noticeably, *e. g.*, 1A6 which contains 6% $Fe_2O_3$ and 4% $SiO_2$ and B10 which contains 6.4% $Fe_2O_3$ and 3.6% $SiO_2$ slaked after 18 days and 2 days respectively. 1A19 (6% $Al_2O_3$ and 4% $SiO_2$) and B20 (6.3% $Al_2O_3$ and 3.7% $SiO_2$) slaked after 5 days and 2 days respectively which tends to show that a slight variation in the ratio of $Fe_2O_3$ to $SiO_2$ has more effect on slaking properties of these mixtures than slight variations in the ratio of $Al_2O_3$ to $SiO_2$. It is also true that slight variations in the ratio of $Fe_2O_3$ to $Al_2O_3$ have a more decided effect than variations of $Al_2O_3$ to $SiO_2$. This is due to the fact as shown by the diagram, Fig. 16, that $Fe_2O_3$ is the least efficient of the fluxes in producing dead-burned dolomite under these conditions.

No outside air slaking test was run on Series B because of lack of material.

## Survey of $Fe_2O_3.Al_2O_3.SiO_2$ Field as Dolomite Fluxes

After the preliminary work, it was decided to run series using $Fe_2O_3$.-$Al_2O_3.SiO_2$ in all proportions that would be practically possible for dead burning dolomite. Four triaxial studies of twenty-two members were made similar to the previous work in 1A blending on the weight basis and using 100-mesh dolomite. Series C consisted of 95% of dolomite + 5% of flux, Series 2A contained 90% of dolomite + 10% of flux, the same as Series 1A. Series D consisted of 85% of dolomite + 15% of flux and Series E consisted of 60% of dolomite + 40% of flux. Series E was made in order to establish the fact that an excess of flux is undesirable. Series 2A was run in order to check up on 1A and also to compare this series with the three new series, it being burned and tested parallel with them.

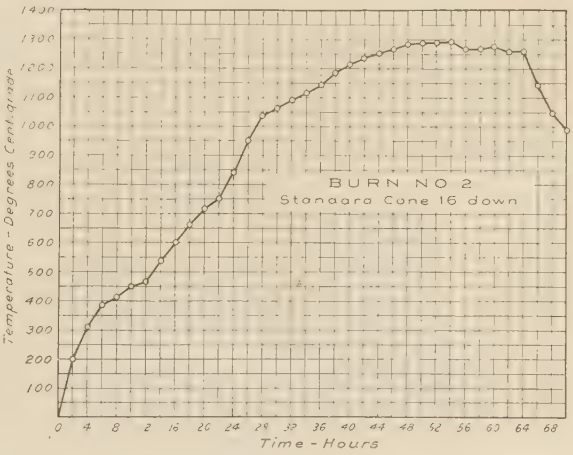



Fig. 18.

The percentage composition of the members of these series is given in Table V. These members were made as previously described for series 1A, using the same oxides as reported.

TABLE V

| Member | Series C 5% Flux, 95% Dolomite $Fe_2O_3$ per cent | $Al_2O_3$ per cent | $SiO_2$ per cent | Series 2A 10% Flux, 90% Dolomite $Fe_2O_3$ per cent | $Al_2O_3$ per cent | $SiO_2$ per cent | Series D 15% Flux, 85% Dolomite $Fe_2O_3$ per cent | $Al_2O_3$ per cent | $SiO_2$ per cent | Series E 40% Flux, 60% Dolomite $Fe_2O_3$ per cent | $Al_2O_3$ per cent | $SiO_2$ per cent |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | 5 | . | . | 10 | .. | .. | 15 | .. | .. | 40 | .. | .. |
| 2 | 4 | 1 | . | 8 | 2 | .. | 12 | 3 | .. | 32 | 8 | .. |
| 3 | 4 | . | 1 | 8 | .. | 2 | 12 | .. | 3 | 32 | .. | 8 |
| 4 | 3 | 2 | . | 6 | 4 | .. | 9 | 6 | .. | 24 | 16 | .. |
| 5 | 3 | 1 | 1 | 6 | 2 | 2 | 9 | 3 | 3 | 24 | 8 | 8 |
| 6 | 3 | . | 2 | 6 | .. | 4 | 9 | .. | 6 | 24 | .. | 16 |
| 7 | 2 | 3 | . | 4 | 6 | .. | 6 | 9 | .. | 16 | 24 | .. .. |
| 8 | 2 | 2 | 1 | 4 | 4 | 2 | 6 | 6 | 3 | 16 | 16 | 8 |
| 9 | 2 | 1 | 2 | 4 | 2 | 4 | 6 | 3 | 6 | 16 | 8 | 16 |
| 10 | 2 | . | 3 | 4 | .. | 6 | 6 | .. | 9 | 16 | .. | 24 |
| 11 | 1.67 | 1.67 | 1.67 | 3.33 | 3.33 | 3.33 | 5 | 5 | 5 | 13.33 | 13.33 | 13.33 |
| 12 | 1 | 4 | . | 2 | 8 | .. | 3 | 12 | .. | 8 | 32 | .. |
| 13 | 1 | 3 | 1 | 2 | 6 | 2 | 3 | 9 | 3 | 8 | 24 | 8 |
| 14 | 1 | 2 | 2 | 2 | 4 | 4 | 3 | 6 | 6 | 8 | 16 | 16 |
| 15 | 1 | 1 | 3 | 2 | 2 | 6 | 3 | 3 | 9 | 8 | 8 | 24 |
| 16 | 1 | . | 4 | 2 | . | 8 | 3 | .. | 12 | 8 | .. | 32 |
| 17 | . | 5 | . | . | 10 | .. | .. | 15 | .. | .. | 40 | .. |
| 18 | . | 4 | 1 | . | 8 | 2 | .. | 12 | 3 | .. | 32 | 8 |
| 19 | . | 3 | 2 | . | 6 | 4 | .. | 9 | 6 | .. | 24 | 16 |
| 20 | . | 2 | 3 | . | 4 | 6 | .. | 6 | 9 | .. | 16 | 24 |
| 21 | . | 1 | 4 | . | 2 | 8 | .. | 3 | 12 | .. | 8 | 32 |
| 22 | . | . | 5 | . | .. | 10 | .. | .. | 15 | .. | .. | 40 |

Six cubes of each member were set on magnesite brick and burned for 64 hours to cone 16 down. The temperature curve for this burn is shown in Fig. 18. The results are shown in Table VI.

As shown by the table, in general the high $Fe_2O_3$ field had what was termed "normal shrinkage;" the high $Al_2O_3$ field possessed the greatest shrinkage and the high $SiO_2$ field, the lowest shrinkage.

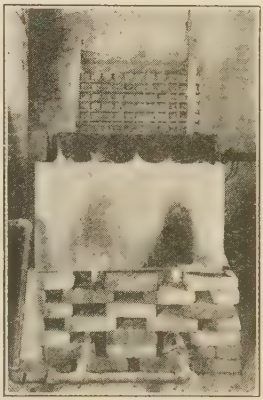


Fig. 19.—Warm water slaking test apparatus.

In Series C, all of the cubes appeared to be of good density and structure. Those containing $Fe_2O_3$ possessed a dull coke-like structure and appearance.

In general, the cubes in Series 2A appeared similar to those in Series C.

The cubes containing $Fe_2O_3$ in Series D appeared to be slightly more dense and vitrified than those in Series 2A. Member D17 had a slag-like appearance due to overfiring, D18 was also glassy due to overfiring. Members D20, D21 and D22 slaked down in the kiln due to an excessive amount of $SiO_2$ which tends to form dicalcium silicate.

The members of Series E all possessed a glassy surface due to overfiring. As shown in Table VI, most of the members of this series were either partially fused or fused down completely. All members were very much overburned showing that 40% of flux is too much for use of the dolomite as a refractory.

Fig. 20.—Autoclave.

Member E19 appeared to be entirely different from any other members studied in that it gave a very white glassy partially fused cube containing long needle-like crystals throughout.

## Tests

The room temperature and outside air slaking tests were run on this series similar to those of the preliminary tests. The hot water test, however, was made more reliable and uniform by using the tank and wire screen basket shown in Fig. 19. This tank contained 47 gallons of water which was maintained constantly at a temperature between 75–85°C. The level of the water was never allowed to fall below the surface of the basket so that the cubes were continuously immersed.

The hot water test under pressure was run in the autoclave shown in Fig. 20. The cubes were placed in the autoclave, filled with water, and heated up to 21 pounds gage pressure, then removed and examined

## Table VI

### Results of Burn at Cone 16 Down

| | Series C | | Series 2A | | Series D | | Series E | |
|---|---|---|---|---|---|---|---|---|
| Member | Color | Remarks | Color | Remarks | Color | Remarks | Color | Remarks |
| 1 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Excessive shrinkage | Reddish brown | Excessive shrinkage |
| 2 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Excessive shrinkage | Brown | Excessive shrinkage |
| 3 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Excessive shrinkage | Reddish brown | Excessive shrinkage |
| 4 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Excessive shrinkage | Black | Excessive shrinkage |
| 5 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Excessive shrinkage | Black | Excessive shrinkage |
| 6 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Low shrinkage, very porous | Fused down completely | |
| 7 | Black | Normal shrinkage | Black | Normal shrinkage | Black | High shrinkage | Black | Partially fused |
| 8 | Black | Normal shrinkage | Black | Normal shrinkage | Black | High shrinkage | Dark brown | Partially fused |
| 9 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Medium shrinkage | Fused down completely | |
| 10 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Medium shrinkage | Fused down completely | |
| 11 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Medium shrinkage | Fused down completely | |

TABLE VI (*Continued*)

| | | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| 12 | Black | Normal shrinkage | Black | Normal shrinkage | Black | High shrinkage | Black | Partially fused |
| 13 | Black | Normal shrinkage | Black | Normal shrinkage | Black | High shrinkage | Brown, glassy | Partially fused |
| 14 | Black | Normal shrinkage | Black | Normal shrinkage | Black | Medium shrinkage | Fused down completely | |
| 15 | Black | Low shrinkage | Black | Low shrinkage | Black | Medium shrinkage | Fused down completely | |
| 16 | Brownish black | Low shrinkage | Black | Low shrinkage | Slaked in kiln to brown powder | | Brown | Partially fused |
| 17 | Light brown | Medium shrinkage | Light brown | High shrinkage | Brown | High shrinkage, very porous | Slaked in kiln to white powder | |
| 18 | Light brown | Medium shrinkage | Greenish brown | High shrinkage | Green, glassy | High shrinkage | Slaked in kiln to white powder | |
| 19 | Brownish green | Medium shrinkage | Pale green | Medium shrinkage | Pale green | Medium shrinkage | White frosty glass, many needle-like crystals present | |
| 20 | Brownish green | Low shrinkage | Green | Low shrinkage | Slaked in kiln | | Slaked in kiln to white powder | |
| 21 | Green | Low shrinkage | Green | Low shrinkage | Slaked in kiln | | Slaked in kiln to white powder | |
| 22 | Yellowish green | No shrinkage | Green | Low shrinkage | Slaked in kiln | | Slaked in kiln to white powder | |

for signs of slaking or cracking. Those which withstood this test were then taken up to 50 pounds gage pressure, then to 97 pounds and finally to 103 pounds gage pressure which was the maximum pressure obtainable in this autoclave. After each pressure interval, the cubes which showed signs of breaking down or cracking were removed.

**Air Slaking Test.**—Both the outside and inside air slaking test proved to be of about the same rapidity in the case of Series C. Member C22 was the first to slake after 70 days' exposure at room and outside temperature. It swelled up to about three times its normal size, finally cracking and slaking down to a powder when pressed between the fingers.

Member C16 after exposure for 92 days in the laboratory, bloated to about $1^1/_2$ times its normal size and cracked badly. After 92 days' exposure outside, it swelled slightly and cracked badly although not as much as did the sample which was left at room temperature. Member C21 swelled and cracked badly after 102 days' exposure both inside and outside, although the sample kept inside swelled slightly more than the outside sample but did not crack as much.

Figure 21 shows these samples together with a cube of the original size before slaking started. The sample of C22 which underwent the outside air slaking test is not shown because it was broken when handled. The three cubes at the top are those which underwent the inside air slaking test, the two in the middle are those of the outside test and the bottom cube is one of original size.

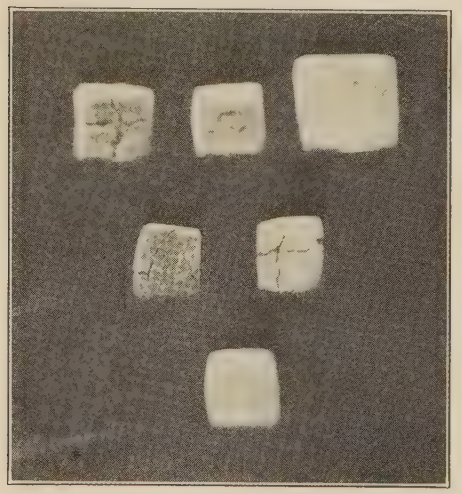


Fig. 21.—Air slaked cubes.

Member C6 slaked inside the room after 131 days but the outside sample has remained O. K. for 150 days.

As shown in Figs. 13 and 14,d several cubes in Series 1A had slaked after standing for 131 days, although Series 2A of the same composition had but one member, 2A1, which slaked both inside and outside after 131 days. After 150 days no other cubes in this series have slaked. This is probably due to the difference in atmospheric conditions. Series 1A was exposed during the summer months when the humidity is high, while Series 2A has been exposed during the winter months of low humidity.

In Series D, Members D15 and D4 have slaked after 131 days' exposure

TABLE VII
WARM WATER SLAKING TEST
Number of Days before Slaking

| Member | Series C | Series 2A | Series D | Series E |
|---|---|---|---|---|
| 1 | 1 | 1 | 1 | 9 |
| 2 | 1 | 1 | 2 | 9 |
| 3 | 1 | 1 | 2 | 21 |
| 4 | 1 | 1 | 1 | 2 |
| 5 | 1 | 1 | 2 | 13 |
| 6 | 1 | 1 | OK after 130 days | Slaked in kiln |
| 7 | 1 | 1 | 1 | Slaked in kiln |
| 8 | 1 | 1 | 2 | 13 |
| 9 | 1 | 2 | 75 | Slaked in kiln |
| 10 | 1 | 2 | 13 | Slaked in kiln |
| 11 | 1 | 2 | 26 | Slaked in kiln |
| 12 | 1 | 4 | 9 | Slaked in kiln |
| 13 | 1 | 13 | 32 | 32 |
| 14 | 2 | 24 | 13 | Slaked in kiln |
| 15 | 1 | 21 | 50 | Slaked in kiln |
| 16 | 1 | 1 | Slaked in kiln | Slaked in kiln |
| 17 | 3 | 2 | 2 | Slaked in kiln |
| 18 | 11 | 2 | 21 | Slaked in kiln |
| 19 | 21 | 5 | OK after 130 days | Slaked in kiln |
| 20 | 1 | 13 | Slaked in kiln | Slaked in kiln |
| 21 | 1 | 2 | Slaked in kiln | Slaked in kiln |
| 22 | 1 | 2 | Slaked in kiln | Slaked in kiln |

inside. No other member of this series has slaked after 150 days' exposure.

No member of Series E has slaked after 150 days' exposure.

**Warm Water Slaking Test.**—The results of this test are shown in Table VII and Figs. 22, 23, and 24.

**Series C.**—In the hot water slaking test, but two members, C18 and C19, appear to be reasonably stable. C18 withstood this test for 11 hours and C19 for 21 hours. Evidently 5% of flux does not give a very wide field of stability. See Fig. 22.

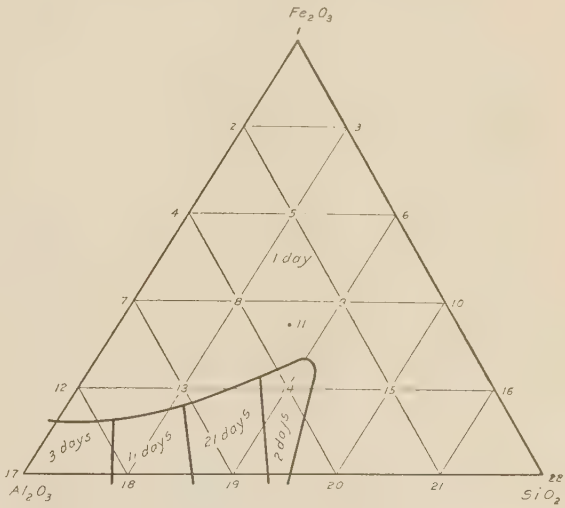



FIG. 22.—Warm water slaking test of Series C.

**Series 2A.**—As shown in Fig. 23, 2A13 and 2A20 were stable for 13 days. 2A15 stood up for 21 days and again as in the preliminary run, Member 2A14 was

the most stable member of the series, slaking after undergoing the test for 24 days.

This test is no doubt more severe than the boiling test conducted in the preliminary run where Member A14 withstood the test for 99 days.

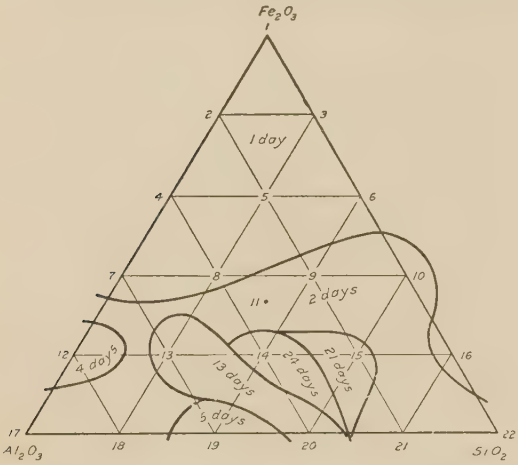



FIG. 23.—Warm water slaking test of Series 2A.

In general, the field around Members 14, 15 and 20 appears to be the most stable as in the case in Series 1A.

**Series D.**—Figure 24 shows that this series possesses a larger field of stability than series C and 2A. The field of low stability in this test lies on the $Fe_2O_3$.-$Al_2O_3$ side especially in the high $Fe_2O_3$ region. The most stable field lies through the center of the diagram away from the apices, the most stable members being D6 and D19 which showed no signs of decomposition after 130 days.

In this series there are seven stable members which underwent this test for more than 20 days. The extreme end members as in the other series, were very unstable.

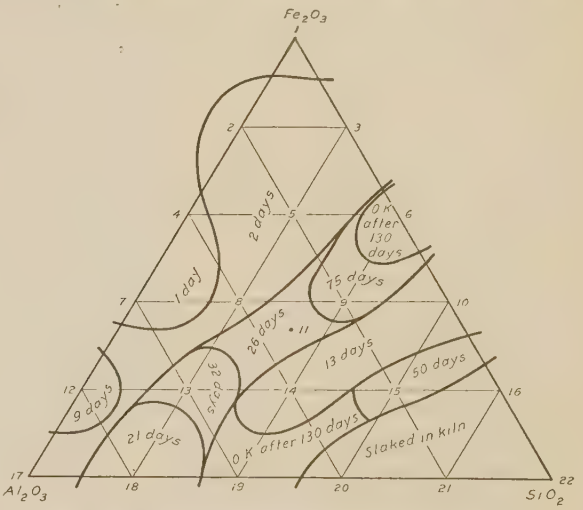



FIG. 24.—Warm water slaking test of Series D.

**Series E.**—In this series, Member E1 stood up for 9 days, E3 was stable for 21 days, E5 and E8 did not slake until after 13 days and E13 stood up for 32 days. Member E19 withstood this test and did not slake after being subjected to this test for 130 days. As previously explained, E19 was partially fused at cone 16 so that it would probably be of no use as a refractory. Also, as previously shown, Member D19 failed to slake after 130 days test in warm water.

Because of the few members obtained in this burn, no definite conclusions on this test can be drawn. However, the tendency seems to be that the region high in $Fe_2O_3$ is again the most unstable.

**Hot Water Test under Pressure.**—The results of this test are shown in Table VIII and Figs. 25, 26, 27.

**Series C.**—The results of this test on Series C are shown in Fig. 25. Here it is seen as in the other slaking tests, the most unstable area is in the high $Fe_2O_3$ field. The members in the low $Fe_2O_3$ region toward the $Al_2O_3$ field appear to be the most stable, Members C13, C14 and C17 did not slake when the gage pressure reached 103 pounds per square inch.

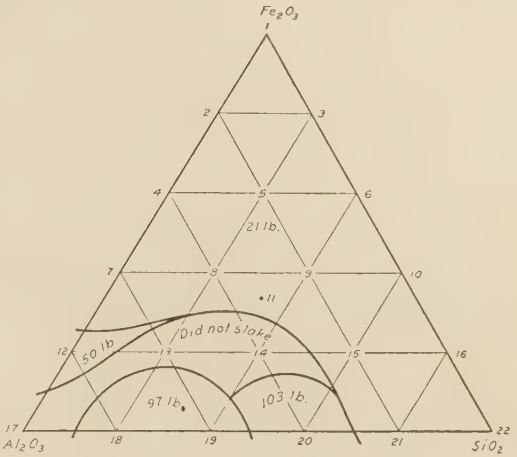



FIG. 25.—Hot water pressure test of Series C.

TABLE VIII

HOT WATER SLAKING TEST UNDER PRESSURE

Number of pounds steam gage pressure applied before slaking

| Member | Series C | Series 2A | Series D | Series E |
|---|---|---|---|---|
| 1 | 21 | 21 | 21 | 21 |
| 2 | 21 | 21 | Did not slake | Did not slake |
| 3 | 21 | 21 | Did not slake | .. |
| 4 | 21 | 21 | 21 | 50 |
| 5 | 21 | 21 | 97 | Did not slake |
| 6 | 21 | 97 | Did not slake | .. |
| 7 | 21 | 21 | 21 | .. |
| 8 | 21 | 21 | Did not slake | 97 |
| 9 | 21 | 97 | Did not slake | .. |
| 10 | 21 | Did not slake | Did not slake | .. |
| 11 | 21 | 21 | Did not slake | .. |
| 12 | 50 | Did not slake | 97 | .. |
| 13 | Did not slake | Did not slake | Did not slake | Did not slake |
| 14 | Did not slake | Did not slake | Did not slake | .. |
| 15 | 21 | Did not slake | Did not slake | .. |
| 16 | 21 | 21 | Slaked in kiln | .. |
| 17 | Did not slake | 21 | 21 | .. |
| 18 | 97 | 97 | Did not slake | .. |
| 19 | 97 | 97 | Did not slake | 103 |
| 20 | 103 | 103 | Slaked in kiln | .. |
| 21 | 21 | 97 | Slaked in kiln | .. |
| 22 | 21 | 50 | Slaked in kiln | .. |

**Series 2A.**—The results for this series are shown in Fig. 26. The unstable field in this series is somewhat smaller than that in Series C but again lies in the high $Fe_2O_3$ area, the stable members lying in the low $Fe_2O_3$ field.

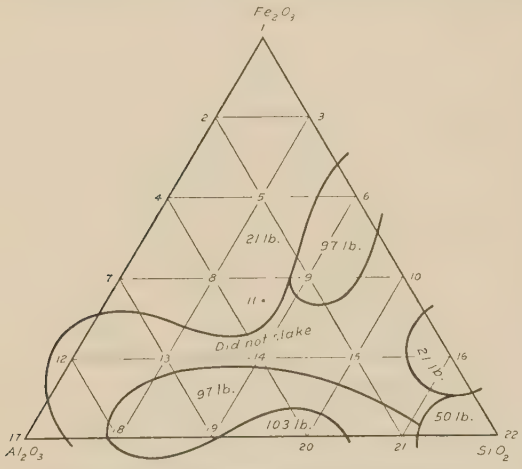



FIG. 26.—Hot water pressure test of Series 2A.

The $Al_2O_3$ content by itself, 10% in 2A17, seems to render the dolomite more unstable than did 5% $Al_2O_3$ in Member C17. Member 2A17 slaked down at 21 pounds pressure whereas C17 did not slake at the maximum pressure used, namely 103 pounds per square inch.

Although Member 2A17 is not included in the most stable area which did not slake in this series, the stable field is larger than that in Series C as will be seen by reference to Figs. 25 and 26.

The stable field lies mostly below the 4% $Fe_2O_3$ of total flux line as is the case in Series C.

The extreme end members are very unstable under this test.

**Series D.**—Fig. 27 shows that 15% flux gives a much larger field of stability than 10% of flux as in Series A. The end members again appear to be very unstable.

Except in Member 2A2, it appears that at least a small amount of $SiO_2$ is required with the fluxes in order to make a stable composition.

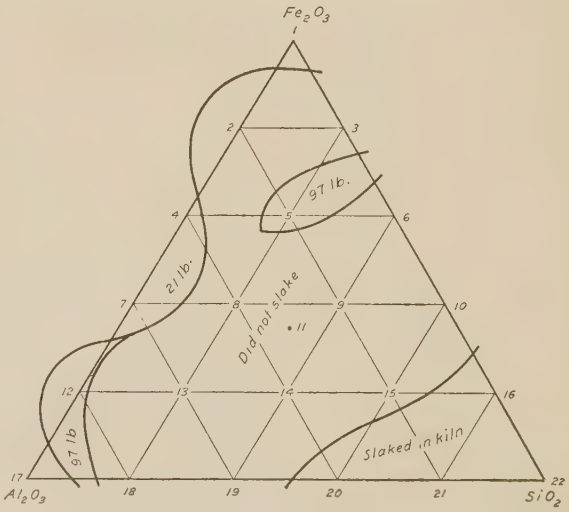



FIG. 27.—Hot water pressure test of Series D.

As was the case in both Series C and Series 2A, Members D13 and D14 did not slake when the maximum pressure of 103 pounds per square inch was attained.

## General Conclusions of Slaking Tests

In all series in these tests except in the test under pressure, two cubes of each member were tested and in every case both cubes slaked together, showing the results to be reliable. Wherever two cubes were used in the tests under pressure, they likewise slaked down together.

It will be noted that as the amount of flux increases, the area of the field of stability becomes larger so that, in general, increase in the amount of flux increases the stability of the dolomite.

Increase in amount of flux not only increases the area of the field of stability, but also the degree or length of time of stability, *e. g.*, the most stable member in Series C stood up in the warm water slaking test for 21 days, in Series 2A for 24 days and in Series D for more than 100 days.

Pure $Fe_2O_3$, pure $Al_2O_3$ or pure $SiO_2$ when used alone are of no value as fluxes for dead burning dolomite.

D6 containing only $Fe_2O_3$ and $SiO_2$ is very stable, likewise D19 containing only $Al_2O_3$ and $SiO_2$ is extremely stable. E19 is very stable, but it contains 40% of fluxes which, as shown later, have too great an effect on lowering the fusion temperature of dolomite to be used as a refractory.

## Fusion Tests

Having determined the field of stability of these oxides as fluxes for dead burning dolomite, it was decided to make a study of the effect of these fluxes on the refractoriness of dolomite in order to determine what stable compounds appear plausible for using as refractories.

*a* *b*

FIG. 28.—Arrangement of cone plaques.

The ordinary cone fusion tests were run on all members of the three series, C, 2A and D. Since Series E appeared to be impracticable for commercial use because of its low fusing temperature as previously described, it was discarded from further work.

These dolomite cones fluxed violently at about cone 26 or lower when placed in the ordinary cone plaques made of sillimanite, bauxite or kaolin; so that it was found necessary to use two cone plaques for each burn. One plaque was made of calcined magnesite to hold the dolomite cones and for the standard cones an ordinary plaque of the following composition:

| | |
|---|---|
| Florida kaolin | 70% |
| Refined alumina | 30% |

This composition was tempered with water, formed into plaques, dried and calcined at cone 9.

The standard cones could not be placed in the magnesite plaque containing the dolomite cones, since it was found that they fluxed with magnesite at about cone 26 or lower.

The magnesite plaques were made of calcined magnesite. They were about $1\frac{3}{4} \times \frac{1}{2} \times \frac{3}{8}$ inches. Three holes about $\frac{3}{16}$-inch deep for holding cones were made in each plaque. These were calcined at about cone 8.

For preliminary tests in order to determine the approximate fusion temperature of the dolomite mixtures, ordinary round plaques 2 inches in diameter by $\frac{3}{8}$-inch deep with holes $\frac{1}{8}$-inch deep containing 8 standard cones ranging from cone 11 to cone 32 were made. These cones were varied with the different fields studied. These round plaques containing the standard cones together with a rectangular magnesite plaque containing three dolomite cones of different composition were placed together, side by side, on a magnesite block in a three-burner compressed air-gas pot furnace. These plaques together with their arrangement are shown in *a*, Figure 28. The furnace used is shown in Fig. 29.

The check determinations were run using 3 standard cones which were set in a sector broken from the ordinary round plaques. These sectors were about $\frac{1}{2}$-inch wide at the center. In many cases, two plaques of dolomite cones with the standard plaque placed between them were used. See *b*, Fig. 28.

The standard cones were held in place in the plaques with alumina powder. The dolomite mixture cones were held in place by powdered 100-mesh calcined magnesite. In order to prevent tipping of the cones, the magnesite powder was thoroughly tamped into the hole around the cone and then built up around it about $\frac{1}{4}$ inch high in order to fill the space formed due to greater contraction, during burning of the dolomite cones in comparison with the magnesite plaques containing them and also due to shrinkage of the magnesite powder itself.

Fig. 29.—Fusion test furnace.

After these details had been adhered to, no trouble was experienced in running these tests.

In many instances, two cones of the same composition were placed in the same plaque and also during checking, cones of similar composition were placed in each of the two opposite plaques in order to assure that the temperature condition in the furnace was the same over the entire area covered by the three small plaques, which, as shown in *b*, Fig. 28, really occupied no wider area than the two plaques used in the preliminary tests.

Also, in several cases, a magnesite plaque containing dolomite cones was placed between two plaques of similar standard cones in order to frequently check on the uniformity of heat in the furnace. Cone 32 was the maximum temperature used in these tests, because of the excessive wear and tear on the furnace at temperatures higher than cone 32.

The cones used in these tests measured $1^1/_2$ inches in length, being made in the standard size cone mold and cut to this length. The standard cones below number 26 were also cut to this length.

## Results of Fusion Tests

**Series C.**—Pure dolomite did not start to deform at standard cone 32 down. In Series C, all cones were standing straight up at cone 32 down, showing that 5% of these fluxes does not harm the deformation point of this dolomite.

**Series 2A.**—The deformation results in series 2A are shown on the triaxial diagram, Fig. 24. The shapes of these dolomite cones, when the standard cones numbered directly below were down, are shown on the diagram. Here it is seen that 10% of $Fe_2O_3$, alone as a flux, caused the dolomite to assume a position of about two o'clock at standard cone 32 down.

Member 17 consisting of 10% $Al_2O_3$ was the softest member of the series, it was down at standard cone 15 down. It started to deform with standard cone 12.

Member 22 containing 10% $SiO_2$ did not start to deform at standard cone 32 down.

There is no single eutectic mixture apparent between the three fluxes in this series, as the diagram shows. The high $Al_2O_3$ field appears to be the softest, the high $Fe_2O_3$ field next and the $SiO_2$ field is the hardest.

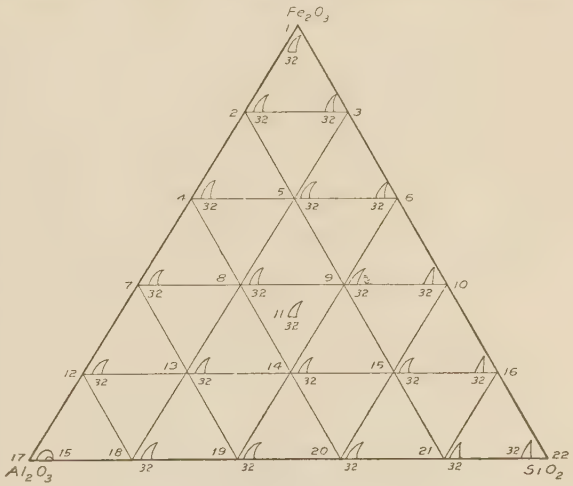



FIG. 30.—Fusion tests of Series 2A.

In every case where the cones stood at about two o'clock when standard cone 32 was down, the dolomite mixture cones started to bend between standard cones 20 and 23. After cone 26 was down, no further bending took place. This is probably explained by the

fact that there was a sufficient amount of eutectic or low-melting mixture of fluxes present, to take enough dolomite into solution to cause the small tip at the top to lose shape and start bending, but the small amount of flux was not sufficiently active to cause the entire mass of dolomite to deform.

A study of the four component systems made up from the 3 component systems $CaO–MgO–SiO_2$; $MgO–Al_2O_3–SiO_2$; $CaO–Al_2O_3–SiO_2$ and $CaO–MgO-Al_2O_3$ given in the introduction, shows that it is to be expected that $Al_2O_3$ would have a more powerful solution action on the dolomite, because of the small field of stability of $Al_2O_3$.

The members along line 1–22 of zero $Al_2O_3$ in Fig. 30 show that $Fe_2O_3$ softens the mixture more than $SiO_2$ since 2A16 and 2A22 are perfectly straight up at cone 32 down while cone 10 is very nearly straight up and cones 2A1, 2A3, and 2A6 are about 2 o'clock at cone 32 down.

The line 2–21 in Fig. 30 shows that 2% $Al_2O_3$ in the presence of 8% of the other two oxides $Fe_2O_3$ and $SiO_2$ has about the same effect on the deformation temperature of dolomite as has 8% $Al_2O_3$ plus 2% of the oxides $Fe_2O_3$ and $SiO_2$ except in the case of 2A21 which has barely started to deform. Member 2A17 which contained 10% $Al_2O_3$ alone as previously mentioned, is much softer than the other members including 2A12 which contains 8% $Al_2O_3$ plus 2% $Fe_2O_3$ and Member 2A18 which contains 8% $Al_2O_3$ plus 2% $SiO_2$. This shows that 2% $Fe_2O_3$ or 2% $SiO_2$ has a decided hardening effect on $Al_2O_3$ as a flux for dolomite. Also since Member 17 in Series C was straight up at standard cone 32 down, the $Al_2O_3$ must be present in quantities over 5% before lowering this dolomite below a refractory of No. 1 grade.

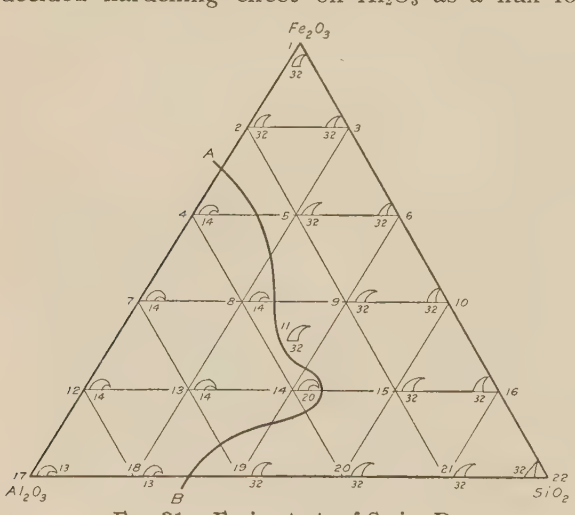



FIG. 31.—Fusion tests of Series D.

**Series D.**—The deformation results in series D which consist of 15% flux plus 85% of dolomite are shown in the triaxial diagram, Fig. 31.

Member D1 containing 15% of $Fe_2O_3$ as a flux had a position of very nearly three o'clock at standard cone 32 down.

Member D22 containing 15% of $SiO_2$ alone as a flux again proved to be the most refractory, being very nearly straight up after standard cone 32 was down.

Likewise, as in Series 2A, Member D17 containing 15% $Al_2O_3$ was again the softest, being down when standard cone 13 was down.

This series compares with Series 2A in that the high $SiO_2$ is again the hardest, the high $Fe_2O_3$ field the next and the high $Al_2O_3$ field the softest.

By comparing the members of this series in the $Al_2O_3$ field to the left of line AB of the diagram, with similar members in Series 2A, it can be seen that 15% of flux where $Al_2O_3$ is present, has a much greater effect on the deformation temperature of dolomite than has 10% of these fluxes. All members in this region were down from standard cone 13 through standard cone 20 down.

Members D17 and D18 came down together, both started to bend when standard cone 10 was just down. Member D12 was slightly slower in deforming than Members D17 and D18.

The members to the right of line AB practically all started to bend between standard cones 20–23 down. After cone 26 was down, no visible deformation took place.

Figure 10 shows that 10% of $SiO_2$ lowers the fusion temperature of pure CaO.MgO from about 2380°C to about 2280°C and 15% $SiO_2$ lowers the fusion temperature to about 2200°C. Likewise, Fig. 9 shows that 10% $Al_2O_3$ lowers the fusion temperature of CaO.MgO from about 2380°C to only 2330°C and 15% $Al_2O_3$ lowers the fusion temperature to only about 2290°C. Comparing this action of $SiO_2$ and $Al_2O_3$, it is evident that 10% and 15% $SiO_2$ lowered the fusion point of pure CaO.MgO more than does 10% and 15% $Al_2O_3$, respectively. These curves cannot therefore be used comparatively as a criterion of the effect of these amounts of fluxes on the lowering of the deformation point of the dolomite studied herein since, as shown, $Al_2O_3$ has much greater effect in lowering the deformation of this dolomite than has $SiO_2$.

Since 15% of $SiO_2$, Member D22, had apparently no effect on the deformation of this dolomite, it may be that the fusion curve of the effect of $SiO_2$ on pure CaO.MgO may agree very closely with that showing the effect of $SiO_2$ on the deformation of this dolomite if this curve would have been determined by using sufficiently high temperatures.

Several members in each series of C, 2A and D were previously calcined to cone 5 and their deformation temperature determined. In all cases the deformation temperature found was the same as when the corresponding raw cones were tested for deformation.

In Series D where 15% of flux was used, there was a tendency for some of the members in the high $SiO_2$ field to form dicalcium silicate and hence decompose. Immediately after removing Members D16 and D21 from the pot furnace after heating to either cone 26 or cone 32, about $^1/_8$-inch of the top popped off the cone and the rest of it immediately slaked down into a fine powder. This happened in every case when these cones were

removed from the furnace. Member D22 which contains 15% of $SiO_2$ alone as a flux did not slake as soon as D16 or D21 after heating to cone 26, but did slake after standing over night, evidently the formation of $2CaO.SiO_2$ was hastened by the presence of 3% $Al_2O_3$ or 3% $Fe_2O_3$.

## Dolomite Bricks

Since member 2A14 gave all indications of being dead burned and contained but 10% of flux, it was decided to study the composition further as to its possibility for making regular size dolomite bricks, using 100-mesh dolomite throughout.

Hand molded briquettes about 5 x 2 x 2 inches were made of this composition. These were burned to cone 16 down. The bricks were set on chrome powder sprinkled over silica bricks, since no magnesite bricks were at hand.

It was found that a very slight dusting had taken place on the bottom, otherwise the bricks came out in very good shape. One of these bricks was tested in the hot water slaking test and remained there 20 days, after which time it broke into 4 pieces. The other bricks were placed outside in the air, where they have already remained for 15 continuous months without any alteration whatever.

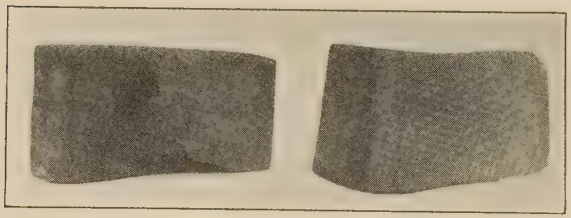


FIG. 32.—RA14 and R1A14.

Large sized bricks, $4^3/_8 \times 8^3/_4 \times 2$ inches, of this composition were made by pressing the bricks out on a hydraulic press using 685 pounds per square inch pressure and 12% water for plasticity. These bricks were burned to cone 17 down and lost approximately 43.6% in weight on the dry weight basis. Both of these bricks cracked during burning. However, they were very firm and dense. They were burned on magnesite brick and no trace of dusting was noted where they came into contact with the magnesite brick.

One of these bricks was heated in an autoclave in water for 2 hours, during which time the gage pressure increased to 65 pounds per square inch. After this treatment the brick was unaffected. It was then again tested in the autoclave at 70 pounds per square inch gage pressure, for two hours at the end of which time it still remained unchanged. This brick RA14 has been standing in the laboratory for 15 months with no sign of alteration. The other brick R1A14 has been standing outside in the open air for the same length of time with no visible change having taken place. These two bricks are shown in Fig. 32.

### Bricks from Calcined Dolomite

**Brick XA14.**—A batch of dolomite was calcined at cone 9. On treatment of this dolomite with hydrochloric acid, no traces of $CO_2$ were given off so that it was assumed that the dolomite was completely free from $CO_2$. According to the analysis of this dolomite, the $CO_2$ amounts to 46.8% by weight so that this amount was deducted from the batch weight which was made up as follows:

| | |
|---|---|
| Dolomite calcined at cone 9..... | 82.66% |
| $Fe_2O_3$..... | 3.47 |
| $Al_2O_3$..... | 6.94 |
| $SiO_2$..... | 6.93 |
| | 100.00 |

Here it is seen that 82.66% of calcined dolomite with the above amounts of fluxes correspond to 90% of raw dolomite plus 10% of fluxes which is the composition of A14.

This batch was mixed with an excess of water and allowed to stand over night in order for the free lime to slake. It was then passed through an 8-mesh screen, sprinkled with $H_2O$ and pressed into a brick about $8^3/_4$ x $4^3/_4$ x $1^9/_{16}$ inches in dimension, using 645 pounds pressure per square in. The water of plasticity on dry basis was 23%. This brick cracked considerably on drying.

**Composition A14Y.**—Determination of the true specific gravity of the raw dolomite by the pycnometer method gave 3.47. A batch of dolomite calcined to cone 5 gave a specific gravity of 3.08 by the pycnometer method, using kerosene as the immersion liquid. According to this specific gravity determination, 90 grams of raw dolomite correspond to 79.89 grams of this dolomite calcined at cone 5. A sample of this dolomite calcined at cone 5 gave no trace of $CO_2$ when treated with HCl and at cone 5 the dolomite should be completely free from $CO_2$ which would give a true specific gravity of 1.85. However, since the determinations for specific gravity checked at 3.08, it was decided to make up several batches assuming that only 11.2% loss in weight, as shown by the specific gravity, had occurred.

The following batch composition was made:

| | |
|---|---|
| c. p. $Fe_2O_3$..... | 2.23% |
| c. p. $Al_2O_3$..... | 4.46 |
| c. p. $SiO_2$..... | 4.44 |
| Dolomite calcined at cone 5..... | 88.87 |
| | 100.00% |

This composition is designated as A14Y.

**Brick X1A14.**—A brick was made of composition A14Y, again using 23% of water as in XA14. This water was added to the mix which was

then allowed to stand for about one-half hour and then pressed into a brick $8^3/_8$ x $4^3/_8$ x $1^{13}/_{16}$ inches at 635 pounds pressure per square inch.

**Brick X2A14.**—This brick was made up of A14Y composition. About 34% of water was added and the mix allowed to stand in a humidor for about 20 hours. It was then screened through an 8-mesh screen and pressed at 370 pounds per square inch pressure into a brick $8^3/_4$ x $4^3/_8$ x $2^1/_8$ inches. This brick required only 200 pounds per square inch for forming because of the fact that it contained such a high per cent of water.

Small white particles of lime were noticeable throughout this brick.

**Bricks X3A14, X4A14 and X7A14.**—Made of composition A14Y except iron oxide analyzing 97.8% $Fe_2O_3$ was used in place of the 99.99% $Fe_2O_3$. This $Fe_2O_3$ was calculated to 100% $Fe_2O_3$ and the corrected amount used. Also, commercial $Al_2O_3$ and $SiO_2$ were used which in both cases analyzed over 99% pure. These bricks were pressed at 550 pounds per square inch.

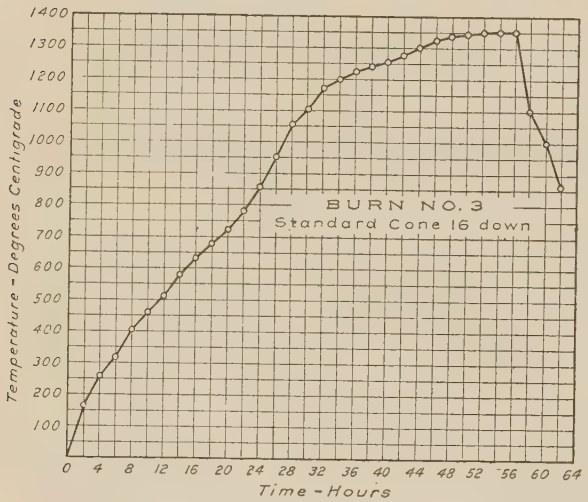



FIG. 33.

**Bricks X5A14, X6A14, X8A14, X9A14, X10A14, X11A14 and X12A14.**—These bricks were made of composition A14Y using 645 pounds per square inch pressure. They were mixed with different percentages of water as shown in Table IX, and pressed into bricks.

### Raw Dolomite Bricks

**Brick R2A14.**—This brick was made of raw dolomite of the same composition as A14 using the C. P. oxides as fluxes. It required 12% of water for plasticity and 610 pounds per square inch pressure before it could safely be removed from the press mold without breaking. With 12% water of plasticity, it was found impossible to obtain a solid brick capable of handling with less than 610 pounds per square inch pressure.

**Bricks R3A14 and R4A14.**—Made of raw dolomite and used the 97.8% $Fe_2O_3$ and commercial $Al_2O_3$ and $SiO_2$, calculating all to the composition of A14. These bricks were treated with 12% of water, allowed

to stand over night in a humidor and pressed into brick at 665 pounds per square inch.

The data regarding all these bricks are given in Table IX. They were burned to cone 16 down according to Fig. 33.

TABLE IX

| Body | Pressure applied to mold. Lbs. per sq. in. | Per cent water of plasticity, dry wt. basis | Per cent volume drying shrinkage (plastic basis) | Condition after drying | Burning loss (dry wt. basis), per cent | Per cent volume burning shrinkage (dry basis) | Condition after burning to cone 16 | Thickness of dry brick in inches |
|---|---|---|---|---|---|---|---|---|
| R2A14 | 610 | 12 | 4.6 | O. K. | 47.0 | 63.8 | Cracked | $2^{7}/_{16}$ |
| R3A14 | 665 | 12 | 8.6 | O. K. | 47.7 | 65.6 | Very good | $1^{23}/_{32}$ |
| R4A14 | 665 | 12 | 4.6 | O. K. | 47.2 | 65.1 | Broken in middle | $1\ ^{7}/_{16}$ |
| XA14 | 645 | 23 | ... | Badly cracked | .... | .... | Badly cracked | $1\ ^{9}/_{16}$ |
| X1A14 | 635 | 23 | 2.7[1] | O. K. | .... | .... | " | $1^{27}/_{32}$ |
| X2A14 | 370 | 34 | 6.5 | " | .... | 64.6 | " | $2\ ^{5}/_{64}$ |
| X3A14 | 550 | 40 | 2.9 | " | 26.7 | 67.2 | " | $2\ ^{1}/_{64}$ |
| X4A14 | 550 | 40 | 0.9 | " | 24.2 | 68.4 | " | $1^{23}/_{32}$ |
| X5A14 | 645 | 40 | 2.3 | " | 26.2 | 72.5 | " | $1^{21}/_{32}$ |
| X6A14 | 645 | 40 | 2.5 | " | 26.9 | 72.0 | " | $2\ ^{1}/_{16}$ |
| X7A14 | 550 | 60 | 5.3 | " | 27.7 | .... | " | $1^{11}/_{16}$ |
| X8A14 | 645 | 21 | 11.3[1] | " | 26.8 | 70.0 | " | $1^{15}/_{16}$ |
| X9A14 | 645 | 40 | 2.9 | " | 29.5 | 73.7 | " | $1^{23}/_{32}$ |
| X10A14 | 645 | 45 | 5.1 | " | 28.7 | 70.4 | " | $1\ ^{7}/_{8}$ |
| X11A14 | 645 | 45 | 7.8 | " | .... | .... | " | $1^{13}/_{16}$ |
| X12A14 | 645 | 45 | .... | " | 27.9 | .... | " | $2\ ^{1}/_{16}$ |

[1] Expansion.

The drying volume shrinkage and burning shrinkage were determined by calculating the volume of the bricks from the measurement of their thickness, width and length, both before and after drying and burning.

**Results of Burn 3.**—Brick R2A14 was cracked through into three pieces and had several horizontal cracks along the bottom side on which it was standing when burned. After standing for about 10 weeks, the bottom along these cracks broke into several small pieces. This brick was no doubt too thick to burn without cracking.

Brick R3A14 was in very good shape. It is a very dense and solid heavy brick, which after 15 months has shown no sign whatever of cracking or slaking in any way. Fig. 34 shows this brick; also R4A14.

Brick R4A14 was broken down through the middle. Otherwise, it resembled brick R3A14 very closely, which was of the same composition. After 15 months' standing in the laboratory, no visible change has taken place in this brick.

All bricks with prefix X on the designation mark, where previously calcined dolomite was used in making the batch, were badly cracked after burning, and had many spots of dicalcium silicate throughout. After standing for about 28 days, all of these bricks slaked and disintegrated. Several of them, after standing in the laboratory and slaking for about eight months, are shown in Fig. 35.

The amount of pressure varied from 370 pounds to 645 pounds per square inch in making bricks with the calcined dolomite mixture, but since all of these bricks were badly cracked, the pressure applied evidently was of no help in preventing this cracking.

Table IX shows that, using raw dolomite, the necessary amount of water required to form bricks sufficiently strong to remove them from the mold without cracking or breaking is 12% of the dry weight of the mixture.

The loss in weight when burning the raw material was about 47%. The theoretical loss due to evolution of $CO_2$ when 90% of dolomite is present is 43%. This leaves 4% loss in weight, about 2% of which is probably due to the dehydration of the $Al_2O_3$ which combines with considerable water probably forming in some cases $Al_2O_3.3H_2O$. This water of hydration is not lost until a temperature of 300°C is attainable. The other 2% is probably chiefly due to volatilization at the burning temperature cone 16.

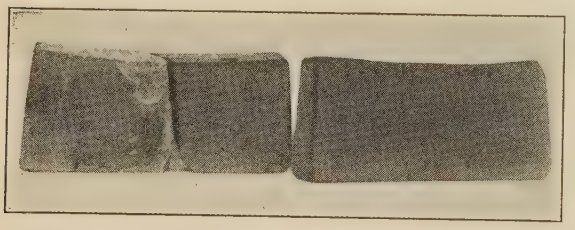


FIG. 34.—R4A14 and R3A14

The burning volume shrinkage is about 65%, which is so excessive that it is practically impossible to make a brick of the raw material on a commercial basis without cracking. As noted, however, brick R3A14 is an exception.

Brick R2A14, which was $2^{7}/_{16}$ inches thick when dry, cracked very badly whereas R3A14 and R4A14, which were only $1^{23}/_{32}$ and $1^{7}/_{16}$ inches thick, respectively, showed a much greater improvement over the thicker brick R3A14, being perfectly solid, and R4A14 being cracked down through the middle. (See Fig. 34.)

Brick XA14 made of dolomite, calcined at cone 9, cracked badly on drying and hence was badly cracked after burning. This brick showed considerable dusting throughout, due to the dicalcium silicate, and after about three weeks it started to disintegrate. After 10 months' exposure in the laboratory, most of this brick had disintegrated.

The increased amount of water required for forming the calcined dolo-

mite mixtures above that required for the raw dolomite mixtures is due to the slaking or chemical combination of water with the free CaO and perhaps MgO in the calcined dolomite.

The loss in weight after burning averages about 27% in the case of the brick made from the calcined material. The theoretical loss due to driving off the chemically combined water from the double salt $Ca(OH)_2$-$Mg(OH)_2$ is 27.2%. Assuming this double salt to be 90% pure, as is the case with these bricks containing 10% of flux, the loss in weight should be 90% of 27.2=24.5%. The cause of the loss in weight of these bricks is thus chiefly due to the loss of chemically combined water and to a slight extent due to the fact that some of the water which combined with CaO was replaced by $CO_2$ while standing in the air before burning. This accounts for the fact that the loss in weight was 27% instead of 24%, as would be the case if no $CO_2$ were taken up by the lime.

Bricks X1A14 and X8A14 were made using only 23% and 21% of water for plasticity, respectively. On drying, these bricks expanded rather than contracted. The water content of these bricks was below 24.5%, which as explained above is the amount required for complete hydration of the CaO and MgO; hence all the water used no doubt went into combination, on standing, of the bricks, leaving no shrinkage water present. Hydration of lime causes expansion.[1] Where more than 24.5% of water was used, the excess shrinkage water present caused a much greater contraction than the expansion caused by the hydration of the CaO and MgO; hence the bricks contracted during drying.

FIG. 35.—Air slaked dolomite bricks.

The average amount of water of plasticity used for making these bricks of previously calcined dolomite was about 40%. In brick X7A14, 60% of water was used. This brick was so badly cracked after burning that its contraction could not be determined. This was also true with bricks XA14, X1A14, X1A14 and X12A14.

The effect of making these bricks under different pressures cannot be drawn from this study since all the bricks of XnA14 composition cracked after burning.

Bricks XA14, X1A14, X2A14 and X11A14 had pieces broken from them in the kiln and could not be weighed after burning.

[1] A. C. Davis, "Portland Cement," p. 201.

In general, it is thus seen that bricks made from the dolomite calcined alone and then adding a flux is impractical due to hydration of the free CaO and MgO.

Bricks made of composition A14 using raw dolomite will no doubt be successful if some means can be found for overcoming the cracking which is due to the high shrinkage.

### Burn 4.—Calcined Plus Raw Material

Several bricks and briquettes of composition A14 which had been exposed to the outside and inside slaking tests were ground to pass a 20-mesh screen.

This crushed calcined dolomite was mixed in a dry pan for two hours with raw composition A14 (100-mesh) in the proportions of 80% of calcined A14 and 20% of raw A14. Also a batch was made using 60% of calcined A14 and 40% of raw A14 composition. These were designated as R20CA14 and R40CA14, respectively.

These compositions were mixed with water and allowed to stand over night. After standing, they became very hard, showing that the calcined material A14 possesses hydraulic properties. These hard batches were then broken and rescreened through an 8-mesh screen. About 20% of water was added and the material pressed into bricks, using 1,000 pounds and 3,000 pounds per square inch pressure. After drying at room temperature for two days, the outside surface cracked badly in all cases. These cracks did not penetrate through the center of the bricks, but only about $^1/_4$-inch deep through the outside surface, which was hard and shell-like due to the fact that it was pressed denser than the inside which was soft and punky. These bricks were again crushed and screened to make the following bricks:

**Brick R40C1A14.**—One half of R40CA14 was treated with 22% of water, rescreened through an 8-mesh screen, allowed to stand 24 hours in a closed vessel and then pressed into a brick using 480 pounds per square inch. This brick was labeled R40C1A14. Although this brick dried without cracking, it was so fragile that when being lifted to place in the kiln, it cracked very badly throughout.

**Brick R40C2A14.**—This brick was made from the other half of batch R40CA14, using 12% by weight of thin coal tar and pressing at 480 pounds per square inch pressure. This brick, however, broke on handling after several hours' standing. It was then disintegrated by hand and after heating for about one hour over a Meker burner, it was treated with 12% of hot tar which when cold was much thicker than the previous tar used. (See analysis, p. 51). However, 12% of this heavy tar proved to be too much, since when pressed to 480 pounds per square inch pressure very little visible compression of the brick took place, due to the large

amount of thick tar and when removed from the die, the brick was of rubber-like consistency. This brick dried without cracking and could be roughly handled without harm.

**Brick R20C1A14.**—This brick was made of composition R20CA14 using 12% of the heavy tar analysis which is given below, and using 480 pounds per square inch pressure. This brick formed very well when pressed with the hot tar and dried without cracking, being very firm and solid, so that it could be easily handled.

**Brick R20C2A14.**—Composition R20CA14 was thoroughly mixed by hand with 7% by weight of powdered caustic magnesite made from Grecian magnesite calcined at 1000°C. The batch taken required 30% of water before it could be successfully molded. Although this brick dried fairly well without cracking, it was so fragile that when being set in the kiln, it cracked throughout.

Tar Analysis

| | Per cent | | Per cent |
|---|---|---|---|
| Bitumen | 77.88 | Specific gravity at 25°C | 1.237 |
| Insoluble organic matter | 22.05 | Float test at 50°C | 2.56 |
| Ash | 0.07 | | |
| | 100.00 | | |

**Bricks X13A14 and X14A14.**—As was mentioned in the description of the preparation of composition A14Y, it was thought that perhaps the dolomite calcined at cone 5 had been completely freed from $CO_2$, although the specific gravity determinations seemed to indicate otherwise. Since bricks made of composition A14Y, assuming that the dolomite was not completely decomposed, had all slaked down, a batch of the percentage composition A14 was made assuming that all the dolomite calcined at cone 5 was completely free from $CO_2$. This percentage composition corresponds to that of XA14 previously mentioned. It was molded into brick X13A14 using 550 pounds per square inch pressure and brick X14A14 which was molded by hand after a sufficient amount of water had been added to make it soggy-like. The amount of water in each case was not measured. Brick X14A14 dried without cracking, while brick X13A14 dried fairly well, but had two small cracks in the center. However, no further cracking occurred with rather rough handling of the bricks.

### Calcined Material

**Compositions A14, D6 and D9.**—Batches of composition corresponding to A14, D6 and D9, all of which stood up against slaking in the air and water, were made. These were calcined to remove all of the shrinkage and then made into large size brick.

The A14 and D6 batches were made by tempering with water into small balls about $1\frac{1}{2}$ inches in diameter. Batch D9 was made into small

circular plaques about $2^1/_2$ inches in diameter and $^1/_2$-inch thick. This was done to determine whether or not the thinner plaques could be more thoroughly calcined than the balls. These were dried and calcined to cone 17 in Burn 2.

The compositions on dry basis of these batches in which C. P. fluxes were used are as follows:

| A14 | | D6 | | D9 | |
|---|---|---|---|---|---|
| Raw dolomite | 90.00 | Raw dolomite | 85.00 | Raw dolomite | 85.00 |
| $Fe_2O_3$ | 2.00 | $Fe_2O_3$ | 9.00 | $Fe_2O_3$ | 6.00 |
| $SiO_2$ | 4.00 | $SiO_2$ | 6.00 | $Al_2O_3$ | 3.00 |
| $Al_2O_3$ | 4.00 | $Al_2O_3$ | 0.00 | $SiO_2$ | 6.00 |
| | 100.00 | | 100.00 | | 100.00 |

**Composition A14C.**—A batch of A14 composition, using commercial materials for fluxes, was also calcined. In this batch North Carolina kaolin of analysis given below was used as the source of $SiO_2$, some $Al_2O_3$ and a slight amount of $Fe_2O_3$. For the deficient $Al_2O_3$, commerical $Al_2O_3$ analyzing over 99% pure was used. For the iron, $Fe_2O_3$ analyzing 97.8% $Fe_2O_3$ was used. The batch weight follows:

| | |
|---|---|
| Raw dolomite | 88.65 |
| $Fe_2O_3$ | 1.92 |
| N. C. kaolin | 8.76 |
| $Al_2O_3$ | 0.67 |
| | 100.00 |

This batch was mixed with water and molded by hand into a briquette about $1^1/_2$ x 3 x 5 inches and also into smaller briquettes about 1 x 1 x 3 inches. These briquettes dried without cracking.

Analysis of North Carolina Kaolin

| | |
|---|---|
| Ign. loss | 16.54 |
| $SiO_2$ | 45.17 |
| $Al_2O_3$ | 37.35 |
| $Fe_2O_3$ | 0.60 |
| $TiO_2$ | 0.03 |
| CaO | trace |
| MgO | trace |
| $K_2O$ | 0.70 |
| | 100.39 |

**Composition D9C.**—This batch was made of the same materials as used in composition A14C, except that all of the $Al_2O_3$ was added in the form of North Carolina kaolin and the deficient $SiO_2$ was added as commercial flint.

The batch recipe follows:

| | |
|---|---|
| Raw dolomite..... | 83.85 |
| $Fe_2O_3$..... | 5.87 |
| N. C. kaolin..... | 7.95 |
| $SiO_2$..... | 2.33 |
| | 100.00 |

The batch was mixed with water and two briquettes $1^1/_2$ x 3 x 5 inches were molded by hand. These dried very well without cracking.

### Results of Burn 4

The burning chart for this burn is given in Fig. 36. In this burn cone 17 was down in the front of the kiln and cone 17 was in the 3 o'clock position in the back of the kiln.

**Brick R40C1A14.**—This brick came out of the kiln badly cracked and bloated. It had a dull-like appearance. The shrinkage was not excessive. (See Fig. 37.)

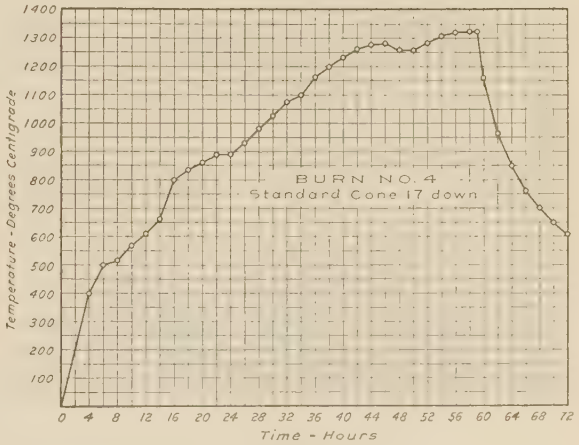



Fig. 36.

**Brick R40C2A14.**—This brick was distorted and badly cracked longitudinally through the center parallel to the face of the brick and also vertically down through the center. The cracking in this case appears to be due more to the method of pressing rather than due to shrinkage which was not excessive. One face of the brick was perfectly smooth and intact so that probably the burning out of the tar binder did not cause all of the cracking, although the vertical disruption appears to be due to this. (See Fig. 37.)

**Brick R201CA14.**—This brick was very badly cracked, broken in two, and bloated. This appears to be due to both the method of pressing and the tar used as a binder. (See Fig. 37.)

**Brick R20C2A14.**—This brick, made using caustic magnesia as a binder, had many cracks, mostly just on the surface. These cracks were formed while the bricks were being set in the kiln, the caustic magnesia not hardening sufficiently to make a tight bond. (See Fig. 37.)

**Brick X13A14.**—This brick had a few cracks which were formed while drying, but evidently did not have any cracks due to burning. This brick was warped. It was very dense, solid and almost glassy appearing. More bricks of this composition were made in the next burn in order to further study its adaptability as a refractory. No dicalcium silicate formed on this brick after standing in the air for 75 days. (See Fig. 37.)

**Brick X14A14.**—This brick had a surface similar to X13A14, but was badly cracked and disrupted. No dicalcium silicate formed on this brick upon standing for 75 days.

These bricks show that it is possible to dead burn previously calcined dolomite if sufficient flux is present. (See Fig. 37.)

**Calcined Material.**—All of these compositions calcined very well except the large briquettes of D9C, about one-half of which dusted down in the kiln. The large briquettes of A14C, however, where the commercial materials were used, proved to be very satisfactory, no sign of dusting or cracking occurring. (See Fig. 37.)

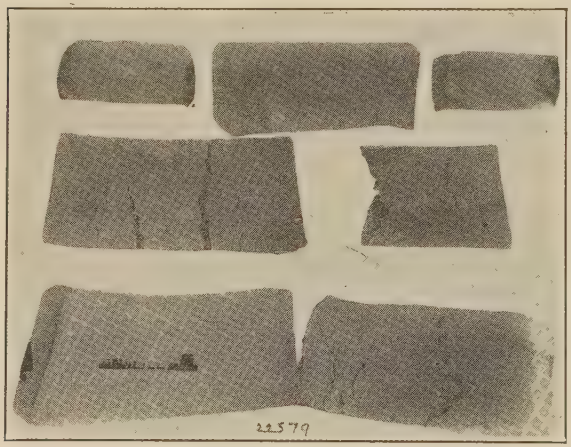


FIG. 37.—Top row, left to right, A14C1, X13A14 X14A14
Middle " " " " R20C2A14, R20C1A14
Bottom " " " " R40C2A14, R40C1A14

## General Conclusions of Burn 4

The use of tar as a bond appears to be of no value, especially when part of the dolomite mixture has been previously calcined. In preparing dolomite-tar mixtures for basic converter linings, Backheuer[1] found that sintered dolomite cannot be used since it prevents absorption of the tar.

The use of water alone in forming bricks of the calcined plus raw material appears to be impossible because of insufficient bonding strength.

Caustic magnesia made from the Grecian variety does not exercise much bonding effect on calcined A14 composition.

Whether or not it is advisable to use a mixture of raw dolomite composition plus calcined dolomite composition cannot be decided from this brief

[1] "The Preparation of the Dolomite-tar Mixture in Thomas (basic converter) Steel Works." *Stahl u. Eisen*, **41**, 954 (1921).

study, although this method of using previously calcined A14 composition, of course, did decrease much of the shrinkage during burning.

Further work done to determine the feasibility of using the calcined dolomite such as composition X13A14 as a suitable material shows it to be impractical. (See Burn 5.)

In using calcined dolomite and then adding the fluxes, a brick molded under high pressure appears to be better than a hand-molded brick.

All of the compositions A14, D6 and D9 will calcine without dusting.

In composition A14 it appears to be possible to use North Carolina kaolin as one of the fluxes in place of free flint and some of the alumina. This kaolin is, of course, much cheaper than the pure oxides for which it is substituted.

Kaolin when used as a flux in composition D9 appears to cause excessive dusting and hence cannot be used.

All calcined bodies seemed to be burned completely through to about the same degree of vitrification so that the shape or thickness used within the limits herein is immaterial for calcining.

### Burn No. 5

The material calcined in Burn 4 was broken in the jaw crusher and run through the disc pulverizer, being ground to the following degree of fineness:

| Mesh | Per cent residue |
|---|---|
| 20 | None |
| 40 | 13 |
| 80 | 30 |
| 100 | 27 |
| 150 | 8 |
| Fines | 22 |

The feasibility of various bonds for use of the calcined material was tried in this burn. The burning curve of Burn 4 was followed throughout except that the temperature was taken to cone 18 down rather than cone 17 down as in Burn 4. This was done in order to bring an even heat throughout the kiln. At cone 17 down, one side was hotter than the other, which had cone 17 deformed to about 2 o'clock.

The methods of preparation of bricks for this burn, together with their drying and burning results, follow. All linear shrinkages given are on the original length basis.

### Starch Paste as a Bond

A very thick starch paste was made by adding a slip of starch in cold water to boiling water and thoroughly stirring.

**Bricks SA14 and S1A14.**—These bricks were made of calcined A14 composition to which was added just enough of the starch paste to make it possible to be molded. Brick SA14 was tamped into the mold by hand. Brickette S1A14 was not a standard size brick as was SA14 but simply a one-inch bar about six inches long molded by hand. These bricks formed very well in the molds, but cracked badly upon drying so that they were not burned.

**Brick SA14C.**—This brick was made of 2,300 grams calcined A14C composition, using 650 grams of starch paste as a binder, and pressed into a standard size brick at 480 pounds per square inch pressure. It pressed and formed very well, but upon drying cracked badly throughout.

It thus appears to be impossible to use starch paste as a bond for calcined A14 composition because of cracking upon drying.

### Magnesium Chloride Solution as a Bond

**Brick MA14.**—Made of calcined A14 composition using a saturated solution of $MgCl_2$ as a tempering medium, enough solution being added to make the mixture soft and plastic so that the brick was made by the soft-mud process. It dried without cracking and burned very well except for a few cracks on the bottom. (See Fig. 38.) The linear expansion from plastic to burned was 1.25%.

**Brick M1A14.**—To 2,000 grams of A14 calcine were added 400 cc. of a 23% $MgCl_2$ solution. This brick was pressed with 460 pounds per square inch pressure. It cracked badly on drying, was rescreened, and, after adding a large excess of the $MgCl_2$ solution it was formed by the soft-mud process. This trial did not crack on drying, but cracked very badly during burning.

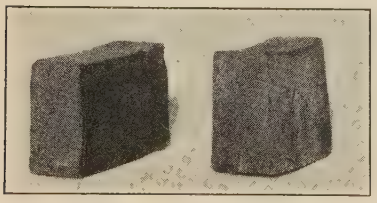


FIG. 38.—Bricks NaD9 and MA14.

**Brick M2A14.**—Made by using calcined A14 composition plus 23% of $MgCl_2$ solution and soft-mud process. This brick cracked on drying and was not burned.

It appears necessary to use a saturated solution of $MgCl_2$ as a tempering medium, otherwise if a dilute solution is used, the bricks crack on drying.

### Caustic Magnesia as a Bond

Caustic magnesia of the California variety, made for use in stucco work, was used.

**Brick EA14.**—This brick consists of calcined A14 composition, 90% by weight plus 10% of caustic magnesia by weight. These were thoroughly mixed and screened. Then sufficient water was added to mold it by the soft-mud process. This brick cracked badly on drying. No bonding

effect whatever seemed to be exercised by the caustic magnesia present, so that this method was discarded and the brick not burned.

### Sorrel Cement as a Bond

An attempt was made to produce Sorrel cement in the calcined dolomite and thus insure a firm bond. This was attempted by using caustic magnesia and $MgCl_2$ solution as shown below.

**Brick M3A14.**—Made by using calcined A14 mixture weighing 1,000 grams, 300 grams of a 14° Bé. $MgCl_2$ solution and 50 grams of caustic magnesia. This mixture was thoroughly tempered by hand and molded by tamping the mixture in the mold. The brick formed well but cracked badly on drying and was not burned.

The reason for cracking was probably due to the presence of sufficient free lime in the calcine to cause the Sorrel cement to disintegrate, as explained by Bole and Shaw.[1] These men state that free lime even in amounts under 2% is detrimental to the life of an oxychloride cement and in quantities over 3% causes early disintegration.

### Sodium Silicate as a Bond

A solution containing 25% of dry sodium silicate by weight was mixed further with water so that the resulting solution contained 4.5% dry sodium silicate by weight.

**Brick NaA14.**—Made of calcined A14 composition tempered with sufficient sodium silicate solution so that the resulting percentage of dry sodium silicate on the A14 calcine weight basis amounted to 0.62%. This brick was molded by hand. It cracked badly on drying and was not burned.

**Brick NaD9.**—Made of D9 composition using sufficient solution to give 0.80% dry sodium silicate. This brick was molded by hand and dried and burned very well. (See Fig. 38.) The brick expanded 1.25% from plastic to burned.

It appears that D9 composition may not be susceptible to this action of cracking during the drying process as is A14 composition.

### Gum Arabic as a Bond

**Brick FA14.**—A thick emulsion of gum arabic was formed by warming an excess of the gum with water. This was cooled and when added to calcined A14 material, it formed small, hard lumps immediately, which made the mass impossible to mold. This material was then heated until it became soft and was then molded by hand. This brick cracked badly immediately upon cooling and was not burned.

[1] "Caustic Calcination of Dolomite and its Use in Sorrel Cements," *Jour. Amer. Ceram. Soc.*, **5** [11], 816 (1922).

## Molasses as a Bond

The heavy "second molasses" obtained from cane sugar was used as a bond.

**Brick BA14.**—This brick was made using 300 grams of molasses to 1,300 grams of A14 calcine. After thorough mixing, a brick was hand molded, which dried and burned very well. (See Fig. 39.) The linear expansion amounted to 1.25%.

**Brick B1A14.**—Made of A14 material using 450 grams of molasses to 2,000 grams of A14 calcine. This molasses was thoroughly mixed throughout and the mixture then pressed at 550 pounds per square inch. The brick formed was very firm and solid. No cracking occurred upon drying at 50°C. It burned very well, but shrunk slightly less on the edge in contact with the magnesite brick support. (See Fig. 39.) The linear shrinkage was 9.3%.

**Brick B2A14.**—This brick was formed of A14 calcine plus molasses and a volume of water equal to that of the molasses. When the water was added to this mixture, it immediately formed small hard lumps. After breaking up the lumps and thoroughly tempering, a brick was tamped in the mold by hand. This brick swelled to a much larger size upon drying and completely disintegrated when an attempt was made to remove it from the mold.

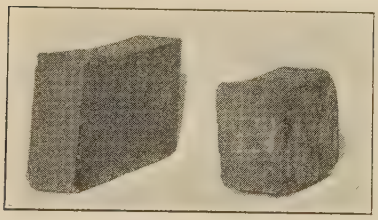


FIG. 39.—Bricks BA14 and B1A14.

**Bricks B3A14, B4A14, and B5A14.**—Those bricks which cracked on drying namely: SA14, S1A14, SA14C, M2A14, M3A14, EA14, NaA14, FA14, and B2A14 were again ground through the rolls and made into bricks using molasses as a bond. These bricks were made using 515 pounds per square inch pressure. They did not crack upon drying, but cracked during the burning process. This cracking was probably due to the fact that the previous bonds containing much water were not driven out before adding the molasses and although no cracks were noticed upon drying after adding molasses, nevertheless the water was still present and strains may have been set up both in the drying and burning process. These bricks were dried over night at 50°F.

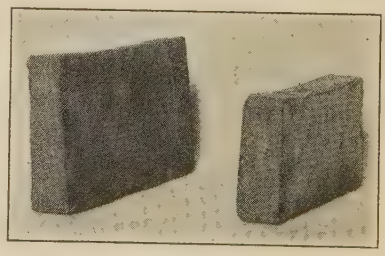


FIG 40.—Bricks DD6 and R6A14.

### Dextrin as a Bond

**Brick DD6.**—Made of 1,500 grams of calcined D6 composition, using 50 grams of thick dextrin paste formed by mixing equal parts of corn dextrin and flour in boiling water until a thick paste was formed. The 50 grams of paste was mixed with 150 cc. of water and after mixing throughout the D6 calcine by hand, was pressed into a brick using 480 pounds per square inch pressure. This brick formed, dried, and burned very well. (See Fig. 40.) Its linear shrinkage was 11.4%.

### Raw Material for Calcine

**Bricks R6A14 and R7A14.**—These bricks were made of composition A14 using raw dolomite (100-mesh) plus C.P. fluxes and mixed with sufficient water to make a very thick slip. They were formed in a standard size wooden mold. These bricks dried in very good condition. R6A14 burned well, similar to brick R3A14 in Burn 3. (See Fig. 40.) It had 28.0 % linear shrinkage. R7A14 fell over against a silica brick and fluxed with it.

**Bricks R1A14C and R2A14C.**—These were made of raw 100-mesh dolomite plus the commercial fluxes including North Carolina kaolin similar to composition A14C (p. 52). R1A14C was molded by the soft-mud process. It dried and burned well except for a small crack clear through the brick. (See Fig. 41.) Brick R2A14C was pressed, using 498 pounds per square inch pressure. It dried very well, but developed three large cracks on burning. The linear shrinkage for R1A14C was 25.7%. The linear shrinkage for R2A14C amounted to 25.7% also.

FIG. 41.—Bricks R1A14C and RA14G.

**Bricks RD6 and R1D6.**—These bricks were made of raw D6 composition. RD6 was pressed at 535 pounds per square inch pressure and R1D6 was hand molded. Both dried well, but cracked rather badly on burning, especially R1D6.

**Brick X15A14.**—Made of composition similar to bricks X13A14 and X14A14 as given earlier in this paper (p. 51). This brick dried well, but cracked badly and was glossy due to overfiring at cone 18.

### Use of Gouverneur Dolomite

In order to determine whether or not other forms of magnesite could be dead burned the same as that from Cedarville, a batch of A14 composition was made using C.P. fluxes and a metamorphosed dolomite or marble from Gouverneur, St. Lawrence County, New York.

The composition of this dolomite, as determined by Bole and Shaw[1] is as follows:

| | |
|---|---|
| $MgCO_3$ | 43.32 |
| $CaCO_3$ | 55.21 |
| $SiO_2$ | 1.00 |
| $R_2O_3$ | 0.46 |
| | 99.99 |

The dolomite was ground to pass a 100-mesh screen, mixed with fluxes, etc., in the same manner as described in the preparation of A14 composition.

Although no sulphur is given in the analysis, the sample evidently contained traces of it, the odor of which could be detected as $H_2S$ when the sample was broken in the jaw crusher. During crushing a very bright, distinct luminescence similar to the well-known triboluminescence of sphalerite was distinctly visible.

**Brick RA14G.**—Unlike the mixture of A14 using Cedarville dolomite, this Gouverneur dolomite mixture was not sufficiently plastic to be molded by the soft-mud process. A brick was made using this A14 composition pressed at 535 pounds per square inch pressure. This brick formed, dried, and burned very well. (See Fig. 40.) It had a linear shrinkage of 28.0%. The appearance of this brick was the same as those of A14 composition made from Cedarville dolomite and after two months' exposure it has remained unchanged.

Thus it appears probably true that any pure dolomite can be dead burned by this process.

### Summary of Satisfactory Brick in Burn 5

This burn shows that suitable bricks when burned to cone 18 down may be made as follows:

1. Calcined D9 composition plus 0.8% sodium silicate. Hand molded.
2. Calcined A14 composition plus 23% of molasses by weight. Hand molded.
3. Calcined A14 composition plus 22.5% of molasses by weight. Pressed at 550 pounds per square inch.
4. Calcined D6 composition plus 13% by weight of a 25% dextrin, 75% water mixture. Pressed at 480 pounds per square inch pressure.

### Burn 6

Magnesite brick are burned while standing on end in order to overcome the lower shrinkage of the edge in contact with the supporting brick. When burned while standing on the 9″ x $2^1/_2$″ edge, magnesite brick always

[1] *J. Am. Ceram. Soc.*, **5** [11], 819 (1922).

shrink less on the edge in contact with the supporting brick and also crack throughout on this edge, so that Burn 6 was made having the dolomite bricks standing on end in order to overcome this distortion noted in Burn 5, where the bricks were burned while supported on edge.

Bricks made of calcined A14 composition, mixed with molasses and burned to cone 17 down in 52 hours are shown in Fig. 42.

**Brick FA14.**—This brick was made of calcined A14 composition, which was ground to give the following screen analysis. (See following page.)

This ground material was pressed into a brick $2^{7}/_{16}''$ x $4^{3}/_{8}''$ x $8^{3}/_{4}''$, using 554 pounds per square inch pressure and 14% of molasses as a binder.

Upon burning to cone 17 down, the brick warped very slightly. It was slightly fused to the magnesia brick on which it stood and shrunk $^{1}/_{4}$ inch less on this end than on the upper end. The edges were very sharp and distinct, showing little or no fusion. The volume shrinkage was 16%, most of which was no doubt due to expulsion of the molasses rather than

| Mesh | Per cent residue |
|---|---|
| 8 | 8.0 |
| 12 | 20.6 |
| 20 | 20.0 |
| 80 | 32.0 |
| 100 | 5.4 |
| Fines | 14.0 |
| | 100.0 |

shrinkage due to vitrification. This brick was very solid and firm, having a sharp ring; the only possible objection being the slightly less amount of shrinkage on the supporting end. (See *a*, Fig. 42.)

**Brick HA14.**—This brick was made of calcined A14 composition ground as follows:

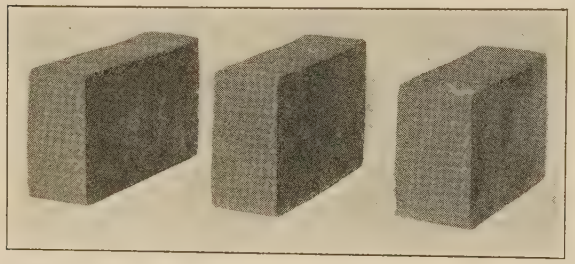
| Mesh | Per cent residue |
|---|---|
| 20 | 0 |
| 40 | 18.0 |
| 80 | 59.0 |
| 100 | 5.4 |
| Fines | 17.6 |
| | 100.0 |

This ground material was pressed into a brick $2^{11}/_{16}''$ x $4^{3}/_{8}''$ x $8^{3}/_{4}''$, using 554 pounds per square inch pressure and 35% of molasses as a binder. This molasses was in excess to what was actually necessary for bonding purposes.

When burned to cone 17 down, this brick did not warp but again shrunk $^{1}/_{4}$ inch less on its supporting end. The edges were very sharp and distinct. The volume burning shrinkage was 25%. This shrinkage is high because of

the high content of molasses used. This brick was very firm and solid, having a sharp ring. (See *c*, Fig. 42.)

**Brick IA14.**—This brick was made of calcined A14 composition, the same as used in Brick $HA_{14}$. The green brick measured $2^{7}/_{16}''$ x $4^{3}/_{8}''$ x $8^{3}/_{4}''$. It was pressed at 554 pounds per square inch pressure, using an unweighed amount of molasses, enough being added to easily work up the batch. This brick fused slightly to the magnesia brick of which it was supported and shrunk $^{1}/_{4}$ inch less on the supporting end. The edges were very sharp and distinct, showing no fusion. The volume shrinkage was 29%. The brick was very solid and firm, having a good ring. (See *b*, Fig. 42.)



*a* *b* *c*

FIG. 42

## Discussion of Burn 6

All three bricks are very good except for the smaller amount of shrinkage on the supporting end. Brick FA14, using coarser grained material, warped slightly. Bricks HA14 and IA14, using finer material, did not warp.

Only those bricks made using molasses as a binder were found to fuse to the magnesia brick. It is believed that this is due to the fact that during the early stages of the burn the molasses gradually seeps down through the brick and runs into the pores of the magnesia supporting brick. This molasses carries a small amount of dolomite with it into the magnesia brick which at higher temperatures causes the slight fusion noted with the magnesia. It was possible to knock these bricks off the magnesia bricks by tapping with a hammer, but a small, skin-like portion of the dolomite brick came off with the magnesia brick. It is suggested that these bricks be set on powdered magnesia spread over the magnesia or silica brick similar to sanding in an ordinary brick kiln to prevent sticking.

## Reasons for Dolomite Stability

An analysis of compositions A14, D6 and D9 made of dolomite plus C.P. fluxes to determine the free CaO or CaO existing therein in the form of possible compounds decomposable by water such as $CaO.Al_2O_3$[1] was made as follows:

The calcined material was crushed and ground to pass a 100-mesh screen. A one-half gram sample was treated with 1,000 cc. of distilled water and thoroughly stirred. This was filtered and the residue washed with dis-

[1] Van Nostrand's *Chemical Annual*, p. 148 (1918).

tilled water until all traces of calcium were removed. The calcium present in the filtrate and washings was precipitated by means of ammonium hydroxide and ammonium oxalate and ignited as CaO.

The results were as follows:

| | A14 | D6 | D9 |
|---|---|---|---|
| CaO | 25.88% | 23.44% | 19.68% |

Thus it is seen that the percentage of free CaO in these calcined dolomite compositions still exists in considerable amounts. The dolomite analysis shows the CaO content to be 30.2%. Since A14 contained 10% of flux and 90% of dolomite, the actual content of CaO in A14 before calcination is 90% of 30.2% or 27.18%; hence but 4.8% of the total lime present has been rendered insoluble when A14 composition is ground to pass a 100-mesh screen. Likewise in D6 composition where 15% of flux is used, the actual lime content before calcination is 25.67% and after calcination is 23.44% so that 8.7% of the total lime present in D6 has been rendered insoluble. A similar calculation shows that 23.3% of the total lime present in D9 has been rendered insoluble by calcination with 15% of flux.

Composition D9 which contains 3% $Al_2O_3$ has more CaO in the insoluble form than D6 which contains no $Al_2O_3$ except the 0.5% impurity as reported in the analysis which makes the total $Al_2O_3$ content of D9 equal 3.4%. The $SiO_2$ content in both is 6%. The $Fe_2O_3$ content in D6 is 9% and in D9 is 6%. As shown in Fig. 1, (p. 11) there are 4 compounds between CaO and $Al_2O_3$. Also the fusion tests tend to indicate a strong fluxing action of $Al_2O_3$ with CaO so that it is probably due to the difference in $Al_2O_3$ content that there is less free CaO in D9 than in D6. Of the possible compounds which could be formed in these mixtures, $CaO.Al_2O_3$ is the only one that could be found in the literature as decomposable by water; hence, no doubt, at least most of the CaO found by this analysis exists as free CaO in the mixture.

Composition A14 contained 4% $Al_2O_3$ but only 2% $Fe_2O_3$ and 4% $SiO_2$ so that it cannot be considered in this method of comparing the action of the different fluxes on D6 and D9.

The slaking of this free lime with water is considered to be the cause of cracking of bricks made from the calcined mixtures when finely ground and tempered with water. A bond tends to overcome this cracking by its binding action, and as shown in bricks DD6 and NaD9 which contain less free CaO than does A14 composition, they are very successful. It is in all probability due to the low water content of molasses that A14 composition can be successfully made into brick.

The question naturally arises as to why these compositions which appear to contain so much free lime are dead burned and do not slake when in

brick form. There are several possible reasons for these phenomena which are given in discussion throughout this work. They are as follows:

1. The condition of approaching the natural composition of Breunnerite is brought about by very intimately mixing the dolomite with $Fe_2O_3$ and grinding very finely so that the MgO forms the stable periclase when calcined. (p. 16)

2. The large amount of MgO present acts as an adulterant and renders the lime inert (p. 19).

3. The lime is overburned, that is, it is burned at a very high temperature cone 17, approximately 1470°C, in the presence of impurities, notably silica, so that it is rendered inactive. (p 17.) These phenomena of overburning are also shown by lime treated with insufficient water to complete hydration. The unslaked portion will "burn" and become practically useless.[1]

4. A dense lime slakes more slowly than a porous lime. (p. 19.) The absorption of cubes A14, D6, and D9 determined by the vacuum method were 0.47%, 2.5% and 2.4%, respectively; showing that these bodies were well vitrified and impervious to the action of water.

5. Compounds may be formed which form an envelope around these CaO grains and prevent them from slaking. Kowalke and Hougen[2] show that in burning magnesia to 1700°C, forsterite ($2MgO\ SiO_2$) crystals form a complete envelope about periclase crystals.

6. It is a known fact that the top layer of fine lime will air-slake (*i. e.*, form $CaCO_3$) and the crust of inert material so formed will prevent access of the air to the quicklime underneath, making fine lime so stable that it can be shipped in open gondola cars.

7. The stability of hydrated lime is likewise attributed to the fact that an impervious coating of air-slaked lime forms on the outside and prevents access of the air to the interior.[3] Chiefly to this cause is attributed the stability of these dolomite compositions. It is considered that a crust or envelope of calcium carbonate is formed around the small particles of free lime present, preventing their contact with water or air, thus rendering them nonsoluble. When finely ground, this protective coating is broken up and the free lime present thus rendered soluble. As stated, the free or water soluble CaO in the product ground to pass 100-mesh ranges as high as 25.88% in composition A14. This water soluble CaO, at least that which exists as free CaO, is thought to be surrounded

[1] W. E. Emley, "Manufacture of Lime," U. S. Bureau of Standards, *Tech. Paper* **16**, 77 (1913).

[2] "Crushing Strength of Magnesia-Silica Mixtures at High Temperatures," *Trans. Am. Electrochem. Soc.*, **33**, 215 (1918).

[3] Emley, *ibid.*, 16–7.

by this impervious air-slaked coating of lime, and is thus inaccessible to the action of water and air.

Absorption tests of samples A14, D6 and D9 at definite intervals for change in weight when soaked in cold water under atmospheric pressure, after having undergone the absorption test under vacuum for one hour, gave the following results.

After soaking for 24 hours, the water in which the briquettes were immersed gave a faint test for CaO. After soaking for 72 hours, the water still gave but a faint test for CaO. The water was then changed and, after remaining in this water for 48 hours, cube A14 did not change in weight, cubes D6 and D9 lost but 0.01 gram in weight. The water gave no test for calcium.

After drying these cubes for 24 hours at 110°C, A14, D6 and D9 showed a decrease in weight from that of their original dry weight equal to 0.39%,

| Hours Soaked | Cumulative Percentage Increase in Weight | | |
|---|---|---|---|
| | A14 | D6 | D9 |
| 24 | 0 | 0 | 0 |
| 48 | 0 | 0 | 0 |
| 72 | 0 | 0.06 | 0.16 |
| 120 | 0 | 0 | 0.08 |

0.49%, and 0.42%, respectively. A slight scum, due to calcium carbonate, was visible on their surfaces.

Analyses for $CO_2$, $H_2O$ and water soluble CaO in samples of A14 composition which had just been removed from the kiln and one which had stood in the air for 12 months were as follows:

| | New sample A14, per cent | 12 months' old sample A14, per cent |
|---|---|---|
| $CO_2$ | 2.87 | 6.03 |
| $H_2O$ | 1.24 | 3.39 |
| Water soluble CaO | 25.88 | 23.76 |
| Theoretical CaO | 27.18 | 27.18 |
| Combined or insoluble CaO | 1.30 | 3.42 |

From the above it is seen that the percentage of $CO_2$, $H_2O$, and insoluble CaO has increased over a period of 12 months. This is due to the formation of carbonates with aging. Evidently more lime has gone into the carbonate form which will, therefore, tend to make the brick even more stable, so that instead of slaking upon standing, this brick will become more resistant to slaking. The percentage of $H_2O$ has increased with aging, probably much of this $H_2O$ is hygroscopic water rather than chemically combined water.

If all of the insoluble CaO were present as $CaCO_3$, the 1.3% of insoluble CaO in the new sample of A14 would require 1.02% of $CO_2$. This leaves an excess of 1.85% $CO_2$, according to the analysis. Likewise, in the

old sample of A14, the 3.42% of insoluble CaO requires 2.69% $CO_2$, thus leaving 3.34% $CO_2$ unaccounted for. It is possible that some of the soluble CaO may be present as the bicarbonate $Ca(HCO_3)_2$; also, no doubt, a small amount of $CO_2$ was left in the product after calcination. Most limestones retain nearly 0.5% of $CO_2$ after calcination in lime kilns.

## General Conclusions

1. In this study, several compositions capable of being calcined at cone 16–17 down, to form apparently dead-burned dolomite, have been found.

2. These stable members together with their compositions are as follows:

| Member | Dolomite % | $Fe_2O_3$ % | $Al_2O_3$ % | $SiO_2$ % |
|---|---|---|---|---|
| B13 | 90 | 3.04 | 5.82 | 1.14 |
| B15 | 90 | 3.62 | 2.31 | 4.07 |
| B21 | 90 | .... | 5.32 | 4.68 |
| B22 | 90 | .... | 4.60 | 5.40 |
| B23 | 90 | .... | 2.98 | 7.02 |
| A14 | 90 | 2.0 | 4.0 | 4.0 |
| A15 | 90 | 2.0 | 2.0 | 6.0 |
| D6 | 85 | 9.0 | .... | 6.0 |
| D9 | 85 | 6.0 | 3.0 | 6.0 |
| D11 | 85 | 5.0 | 5.0 | 5.0 |
| D13 | 85 | 3.0 | 9.0 | 3.0 |
| D15 | 85 | 3.0 | 3.0 | 9.0 |
| D18 | 85 | .... | 12.0 | 3.0 |
| D19 | 85 | .... | 9.0 | 6.0 |

3. Of these members, the following can be classed as Number 1 refractories: *i. e.*, their fusion point lies above standard cone 32, which deforms at about 1770°C; B13, B15, B21, B22, B23, A14, A15, D6, D9, D11, D15 and D19.

4. Any of these compositions could, no doubt, be used as dead-burned granular dolomite.

5. These compositions are made of materials ground to pass a 100-mesh screen and thoroughly mixed before calcination.

6. Composition A14 can be made satisfactorily using North Carolina kaolin as a source of the $SiO_2$ and most of the $Al_2O_3$.

7. Composition D9 cannot be made using North Carolina kaolin because of slaking due to calcium orthosilicate ($2CaO.SiO_2$) formation.

8. As the percentage of flux increases up through 15%, the number and stability of the calcined dolomite flux mixtures increase.

9. Five per cent of the three fluxes $Fe_2O_3$, $Al_2O_3$ or $SiO_2$ is insufficient to produce a dead-burned product from this dolomite.

10. Dead-burned dolomite cannot be obtained using any one of the three fluxes $Fe_2O_3$, $Al_2O_3$ or $SiO_2$ alone in amounts of 5%, 10%, 15% and 40%.

11. Pure dolomites of different crystalline character can be dead burned.

12. All compositions containing 5% of fluxes have deformation points above cone 32.

13. All compositions containing 10% of fluxes have deformation points above cone 32, except the composition A17 containing 10% of $Al_2O_3$ alone as a flux which deforms at cone 15.

14. When 15% of the fluxes studied herein are present, compositions with fusion temperatures at cone 20 or lower are obtained when the total $Al_2O_3$ content exceeds 6% and $Fe_2O_3$ is present.

15. $Al_2O_3$ has by far the greatest effect in lowering the fusion temperature of this dolomite. $Fe_2O_3$ is next and $SiO_2$ has the least effect on lowering the fusion temperature.

16. These dolomite compositions without molasses will not flux with magnesite below cone 33 as shown by the fusion tests.

17. It is very difficult to make commercial sized bricks of the raw material because of the excessive volume burning shrinkage which at cone 16–17 down, averages about 70% on the dry volume basis. This high shrinkage causes cracking and deformation of the bricks.

18. Using previously calcined dolomite and then adding the fluxes and calcining is of no value because of high shrinkage due to hydrated lime.

19. Dolomite brick can be made satisfactorily as follows:

Calcine the raw materials of the compositions below to cone 17 down. Grind to pass a 20-mesh screen. Form into bricks and burn to cone 17–18 down.

Raw Batch Recipe

| | $A_{14}$ | $D_6$ | $D_9$ |
|---|---|---|---|
| 100-mesh dolomite | 90 | 85 | 85 |
| $Fe_2O_3$ | 2 | 9 | 6 |
| $Al_2O_3$ | 4 | .. | 3 |
| $SiO_2$ | 4 | 6 | 6 |

Method I—A14 composition plus 16%–23% of molasses by weight. Mold by hand or press at 550 pounds per square inch.

Method II—D6 composition plus 13% by weight of a 25% dextrin, 75% water mixture. Press into brick at 480 pounds per square inch.

Method III—D9 composition plus 20% of a 4.5% sodium silicate solution. Mold by hand.

20. When using 100-mesh raw Cedarville dolomite, water serves very well as a bond for a standard size brick.

21. Artificial bonds containing a high percentage of water cannot be used for making bricks of composition A14 because of cracking during the drying stage.

22. Cracking of the fine calcined material during drying is due to hydration of the free lime.

23. Compositions D6 and D9 do not appear to have the fault of cracking during drying when much water is used in the bond.

24. Tar appears to be unsatisfactory for bond for the calcined material, although it contains no water.

## AUTOBIOGRAPHY

I, James Thomas Robson, was born in Cleveland, Ohio, February 1, 1895. I received the first three years of my grammar school education in the public schools of the city of Cleveland, Ohio, and the remainder of my secondary school education in the public and high schools of the city of Elyria, Ohio; my undergraduate education at the Ohio State University from which I obtained the Degree of Bachelor of Chemical Engineering in 1919 and the degree of Master of Science in 1920. While in residence at the Ohio State University, I acted in the capacity of Student Assistant to Prof. C. W. Foulk from 1916 to 1918, as Student Assistant to Dr. James R. Withrow from 1918 to 1919. In 1919 I was appointed part-time instructor in Ceramic Engineering at the Ohio State University and continued my graduate work until 1923 when I received from the Ohio State University the Degree of Doctor of Philosophy.